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AN EXPERIMENTAL STUDY OF
MECHANICAL AND DIELECTRIC LOSSES
IN CERTAIN HIGH POLYMERS

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Final Report

JANUARY 1959

Contract No. Nonr 401(09), Task No. NR 330-026

Principal Investigator: H. S. Sack

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Chemistry Branch
OFFICE OF NAVAL RESEARCH
Washington, D. C.



CORNELL UNIVERSITY
Department of Engineering Physics
Ithaca, New York

AN EXPERIMENTAL STUDY OF
MECHANICAL AND DIELECTRIC LOSSES
IN CERTAIN HIGH POLYMERS

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Final Report prepared by:

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January 1959

Contract No. Nonr 401(09), Task NR 330-026

Chemistry Branch
Office of Naval Research
Washington 25, D. C.

ABSTRACT

Second-order transitions in pure polyvinyl acetate, cellulose acetate pure and plasticized, cellulose nitrate pure, plasticized, plasticized and stabilized, and plasticized and cross-linked were studied using both mechanical and dielectric loss measurements. In the study of mechanical losses, the main effort was directed towards low frequencies, and equipment was designed which permitted measurements down to about 10^{-4} cps. Temperatures as low as -200°C were used in some cases. The techniques made use of forced torsional oscillations or of a torsion pendulum. The results were expressed in terms of the complex modulus $G_2' + iG_2''$, and G_2' and G_2'' were plotted as functions of temperature. The peaks in the curves of G_2'' gave temperatures characteristic of the transitions. From these, activation energies were obtained.

Dielectric measurements were made at higher frequencies, i.e., 60 cps to 2 mc. The dielectric constant was measured as a function of temperature and from the positions of the peaks of these curves graphs of $\log f$ versus $1/T_{\text{max}}$ were obtained, and the activation energies computed. These measurements, though at higher frequencies, provided a useful comparison.

Emphasis was put on finding the location of these peaks and their shifts with frequency, plasticizer and cross-linking, etc. No effort was made to compare the complete curves over the whole temperature range.

Since the location of the peak on the temperature scale is dependent on the preparation of the test specimen and since there are often several peaks, the corresponding peaks occurring at different frequencies were distinguished by their activation energy.

For polyvinyl acetate the observed activation energy of ~ 57 KCal/mole, in agreement with Meeds and Fuoss²⁰, increased to ~ 120 KCal/mole at the very low frequencies.

It is found that the activation energy is not constant with temperature but increases as the static transition temperature is approached. Examples are polyvinyl acetate, pure cellulose nitrate and some of the plasticized samples.

No basic difference could be found in the dielectric behavior of cellulose triacetate and cellulose 2.3 acetate. Activation energies of ~ 35 to 45 KCal/mole were obtained.

The addition of a plasticizer does not change radically the value of the activation energy for any particular transition, but only shifts the peaks to lower temperatures. This shift becomes relatively smaller as the plasticizer content continues to increase. Variation of plasticizer content in cellulose nitrate from $\sim 5\%$ to $\sim 6\%$ increased the activation energy from ~ 23 to ~ 50 KCal/mole.

The addition of a stabilizer makes the measurements more consistent and reproducible. Its presence reduces the activation energy; the effect is similar to that produced by a cross-linking agent.

Contrary to expectation, cross-linking reduces the value of the activation energy as observed from dielectric measurements. Its presence did not make any appreciable difference in the mechanical measurements. However, in both cases, the transition peaks shift to lower temperatures

Plasticised samples are found to be rather unstable. It is suspected that the plasticizer evaporates during the experiments, thus often leading to incorrect results. This erratic behavior renders it difficult to make precise statements.

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I. INTRODUCTION

Among the many properties of high polymers, the so-called "second-order transition" has received a great amount of attention. The transition temperature--or better, the transition region--is that narrow region in which various physical properties exhibit a discontinuity in variation with temperature. In particular, the specific heat shows anomalies at, or around this point, giving rise to a curve as a function of temperature resembling the "lambda" curve so well-known in order-disorder transitions in metals (e.g. brass), in hydrogen halides and other substances. Because of this similarity the name "second-order transition" has also been used for the apparently similar phenomena in high polymers.

According to the generally accepted usage of the words, a first order phase transition such as crystallization or vaporization involves a discontinuity in the primary thermodynamic variables like volume, energy or entropy when described as a function of temperature. A second-order transition, however, is characterized by a sudden change in the first derivatives of the thermodynamic variables. In other words, the second-order transition involves intensive¹ properties like thermal expansivity, refractivity, specific heat or compressibility, etc. An investigation of the behavior of any of these intensive properties provides information about the second-order transition.

The second-order transitions are considered true thermodynamic transitions in the sense that they are describable in terms of the variables energy, entropy and temperature. They have the character of cooperative

phenomenon, and their quantitative theoretical treatment has made considerable progress.² Many models that have been used lead to well-defined transition temperatures.

However, there are marked differences in the behavior of high polymers and metals, e.g., in the second-order transition region. The most common method for determining the transition temperature is the volumetric method: when the volume is plotted as a function of temperature, the slope shows a discontinuity at this temperature. A great number of high polymers have been studied in this way and gave evidence of one or even more than one transition temperature.* It is worthwhile noting that in many cases the change in slope is on the borderline of experimental certainty, and sometimes the measured points could also be represented by a curve instead of a broken line. Furthermore, the point is sensitive to the constitution of the polymer and the specific heat curves are more gradual than in the case of "classical" second-order transitions. It is also striking that in the same temperature region a softening of the material occurs, and that it changes from a brittle to a soft substance (as the temperature is raised). This transition is thus also called the "glass-liquid" transition. On the basis of these facts, the transition already had been related at an early time to the onset of rotation of the polymer molecules⁴ and was sometimes compared with the onset of rotation as observed in the second-order transition of hydrogen halides and paraffins.

Among the first to point to an essential difference between the transitions in high polymers and classical second-order transitions were

*For a summary of early data see, for example, Boyer and Spencer;³ for examples of more than one transition see later in this thesis.

Alfrey, Goldfinger and Mark⁵ who, in their investigation on polystyrene, found a time dependence of the second-order transition point. According to these authors the transition then merely represents the temperature where the rate of attainment of equilibrium or the relaxation time of some internal mechanism is of the order of the time scale of the experiment. Thus this type of a second-order transition seems to be determined by a rate process rather than by a true thermodynamical phase change. In fact most synthetic polymers show rotation around the bonds of the chain backbone. The rotations are hindered by the potential barriers. When the thermal energy becomes great enough, rotation begins. Earlier Fuoss⁶ had suggested that this rate process was responsible for the peaks in the dielectric loss curves which he observed in polyvinyl chloride and other polymers having polar groups. He also pointed to the relation of his observation to the second-order transition.

Among the first to correlate the transition point with mechanical loss were Sack⁷ and his associates. Loss peaks were observed similar to those found with dielectric measurements. Since the occurrence of elastic losses is not bound to the polar groups, this method permits the study of non-polar substances also. Furthermore, since mechanical measurements can be made easily at very low frequencies, they may be useful in extending the frequency range. Since the work of Sack and his associates, the study of mechanical losses has become a useful tool in the investigation of second-order transition in high polymers. The present investigation is a further experimental contribution to this field, with particular emphasis on the influence of plasticizing and cross-linking.

The presence of a plasticizer increases the mobility of the chains and, since the second-order transitions are related to mobility of the polymer chains, their occurrence is influenced by the addition of the plasticizer. Boyer and Spencer⁸ give an equation relating the polymer fraction W_2 in a plasticized polymer to its activation energy E as

$$\text{Log } \eta = A + B\sqrt{W_2} + \frac{E}{RT}$$

Assuming the conditions of isoviscous state, the viscosity η is taken to be constant. Then

$$W_2 = D - \frac{E}{RT}$$

where A , B and D are constants, T the absolute temperature and R the gas constant. The equations are not strictly correct because the activation energy E itself changes with the addition of a plasticizer.

Kauzmann⁹, in his investigations on polyvinyl chloride, found that the activation energy decreased with an increase in plasticizer content.

In particular, Boyer and Spencer have drawn a curve--based on the work of Uberreiter¹⁰ on nitrocellulose plasticized with various amounts of tricresyl phosphate--of the square root of the polymer fraction W_2 against the reciprocal of transition temperature T_g . According to these authors, "the first few percent of the plasticizer produce a rather marked lowering of T_g and represents a saturation or neutralization of the hydroxyl groups along the cellulose chain. The more gradual decrease in T_g which follows may then signify a neutralization of other polar groups." Uberreiter obtained a transition temperature of 40 C for his pure nitrocellulose. With 10%, 40% and 60% of tricresyl phosphate the transition temperature moved down to +3°C, -30°C and -43°C respectively. These values were obtained from volume temperature curves. Such curves do not describe the frequency dependence.

Bueche,¹¹ from his measurements of viscous flow of polystyrene of varying concentrations in solution in diethyl benzene, has computed the values of the activation energy as a function of the concentration. According to this investigator the activation energy varied from 2 to 100 kcal./mole in going from the pure solvent to the pure polymer.

The present work was undertaken in order to gather more information about the second-order transition, in particular with respect to its dependence on frequency and the degree of plasticization and cross-linking, etc. It is a continuation and extension of the investigations by Woods,¹² who studied several high polymers including pure cellulose nitrate. He compared the viscoelastic behavior with the dielectric behavior of each polymer, a procedure that was also followed throughout the present work. Woods found that for cellulose nitrate the corresponding transitions for viscoelastic behavior occurred at higher temperature than those for the dielectric behavior. However, the activation energy was the same in both cases and was equal to about 4.6 kcal./mole. The transition at the lowest frequency (50 cps in mechanical measurements) occurred at -70°C which is very different from a value expected on the basis of Uberreiter's experiment at zero frequency.

The investigations reported herein consist in the study of the dielectric and elastic losses of samples of cellulose nitrate, pure and plasticized and cross-linked to various degrees, of pure and plasticized cellulose acetate and of pure polyvinyl acetate. Woods' work had shown that elastic losses versus temperature curves for polyvinyl acetate showed peaks in a region close to but above room temperature for frequencies of 1 cps or more. It was interesting, therefore,

to extend these measurements to still lower frequencies. Dr. Flory and his associates of Cornell University Chemistry Department had studied cellulose acetate and it was of interest to be able to compare results. Cellulose nitrate, being one of the cellulose derivatives exhibiting more than one transition and characterized by relatively large side chains, was of interest because the influence of plasticization and cross-linking could be substantial. It had been studied with regard to other properties by Dr. Newman and Dr. Drochael from the Hercules Powder Company.

Since different techniques were used in the different frequency regions, the results are represented in a form independent of the constants of the apparatus. This was achieved by interpreting the experimentally obtained quantities in terms of the real and imaginary parts of the modulus. Thus plots of G_2' and G_2'' against temperature are given throughout this thesis. From the positions on the temperature scale of the peaks of G_2'' for various frequencies, the activation energies for the samples were obtained.

A maximum temperature range of -170°C to $+130^{\circ}\text{C}$ has been covered. However, not all the samples have been studied over this whole range. For example, the plasticizer would evaporate at a rapid rate at the higher temperatures. In general the plasticized samples were not stable over very long times, but showed definite drifts towards a lower plasticizer content.

A frequency range of 10^{-3} cps to 10^2 cps was covered for mechanical measurements. For electrical measurements, however, the frequency was much higher; from 60 cps to 2 mc.

II. TEST SPECIMENS

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The various high polymer samples which were investigated during the work described here are listed in the table on pages 9 and 10.

The polyvinyl acetate had been prepared and used by Woods¹² in his measurements. Cellulose 2.3 acetate pure and with "M-17 santicizer" and cellulose triacetate pure and plasticized with metacresol were prepared by Messrs. Russell and Van Karpel of the Cornell Chemistry Department.* All these samples were prepared by pouring solutions of the high polymers on a mercury surface, drying with dry air the film that formed, and then waterleaching and drying them again in an oven.

The cellulose nitrate samples had been specially prepared by Dr. S. Newman and his associates at the Hercules Powder Co.† In general these samples were obtained by spreading a solution on a horizontal plate and leveling it to an even thickness by means of parallel blades. These samples were much smoother in appearance and more even in thickness than those of Woods and Russell.

For the dielectric measurements, disks of $1\frac{1}{8}$ " diameter were cut from these samples by a punch. Most of these samples were gold plated on both sides for better surface contact with the electrode plates. For the process of coating, the disks were covered with aluminum masks covering a belt of $\frac{1}{16}$ " width

* The author wishes to thank Dr. J. Russell and Dr. R. G. Van Karpel for their help in providing these samples.

† The author wishes to express his appreciation and thanks to Dr. S. Newman and associates for specially preparing these samples.

along the rim, and then goldplated by evaporation in vacuum. The samples were kept about 11" from the heater in order to minimize any loss of the plasticizing agent. The samples from the Hercules Powder Co. were smooth enough so that the softer samples could be used uncoated without impairing the contact with the condenser electrodes. The gold plated samples were stored in a desiccator to keep them dry.

The samples for the mechanical measurements were cut in the form of strips of approximately 5 cm x 1 cm. Those with a higher elastic modulus were cut somewhat narrower.

The stock samples were enclosed in plastic bags and kept at room temperature.

The plasticizer metacresol crystallizes at $+8^{\circ}\text{C}$ and boils at 217°C whereas N-17 plasticizer crystallizes at -40°C and boils at 345°C . For most of the plasticized cellulose nitrate samples diethyl phthalate was used. Two samples were plasticized by the more stable di(2-ethyl hexyl) phthalate. The cellulose nitrate for these two samples was taken from a different batch.

COMPOSITION OF SPECIMENS

NO.	POLYMER	COMPOSITION	PERCENTAGE OF PLASTICIZER	PERCENTAGE OF CROSS-LINKING
1	Cellulose secondary acetate	Cellulose 2.3 acetate	100	-
2	Cellulose secondary acetate	Plasticized with M-17 stabilizer	50	50
3	Cellulose triacetate	Cellulose 3.0 acetate	100	-
4	Cellulose triacetate	Plasticized with metaresol	50	50
5	Polyvinyl acetate		100	-
6	Cellulose nitrate 443-37	12.6% nitrogen nitro-cellulose	100	-
7	Cellulose nitrate 443-60-A	Cellulose nitrate plasticized with diethyl phthalate	95.2	4.8
8	Cellulose nitrate 443-60-B	Cellulose nitrate plasticized with diethyl phthalate	83.3	16.7
9	Cellulose nitrate 443-37-B	Cellulose nitrate plasticized with diethyl phthalate	58.6	41.4
10	Cellulose nitrate 443-37-A	Cellulose nitrate plasticized with diethyl phthalate	50.1	49.9
11	Cellulose nitrate 443-37-C	Cellulose nitrate plasticized with diethyl phthalate	39.3	60.7

COMPOSITION OF SPANJENS (cont'd)

NO.	POLYMER	COMPOSITION	POLY- MER	PLASTI- CIZER	CROSS- LINKING	DEGREE of CROSS- LINKING
12	Cellulose nitrate 443-61-A(72)	Cellulose nitrate plasti- cized with diethyl phthalate and cross-linked with HDI	48.8	48.8	2.44	.70
13	Cellulose nitrate 443-61-B(72)	Cellulose nitrate plasti- cized with diethyl phthalate and cross-linked with HDI	49.3	49.3	1.47	.62
14	Cellulose nitrate 443-61-C(72)	Cellulose nitrate plasti- cized with diethyl phthalate and cross-linked with HDI	49.6	49.6	.74	.18
15	Cellulose nitrate 443-61-C(49)	Cellulose nitrate plasti- cized with diethyl phthalate and cross-linked with HDI	49.6	49.6	.74	.06
16	Cellulose nitrate 333-59-A	Cellulose nitrate plasti- cized with di(2-ethyl hexyl) phthalate	50	50	-	-
17	Cellulose nitrate 333-59-B	Cellulose nitrate plasti- cized with di(2-ethyl hexyl) phthalate and stabilized with 1% stabilizer	50	49	-	-

III. EXPERIMENTAL PROCEDURES

A. Mechanical Measurements.

All measurements were made with sinusoidally varying stresses. Three different techniques were used for different frequency regions, namely, frequencies much lower than 1 cps, of the order of 1 cps, and much higher than 1 cps. In many cases the strain amplitude was varied and it was found that the results were independent of this parameter. Thus it is permissible to treat the sample as a linear visco-elastic material, and to describe the elastic behavior under the periodic loading by a complex elastic modulus.

a. Low Frequency Region. (less than 1 cps.)

The low frequency response was studied by means of forced torsional oscillations. The principle of this method is similar to one used by Philippoff¹³, though the instrument itself is quite different. The plastic sample in the form of a thin narrow strip was attached at its upper end b (see figure 2) to a copper wire stretched vertically above it. The lower end c of the specimen was clamped to a rigid support. A sinusoidally varying torque was applied to the upper end a of the wire and was transmitted through the wire to the sample. Due to the viscous damping of the sample the angular displacement of its upper end b lags behind that of the upper end of the wire. Thus a phase difference ψ exists between the angular displacements of a and b, which is a measure of the damping. This angle can be obtained in two different ways. If the motion of a and b is projected simultaneously by means of two light beams on a common scale, then the two light spots

will cross twice during each cycle. This "cross-over point" can be recorded and from it Ψ can be calculated. From fig. 3 it is seen that if θ_1 is the angular displacement of a, and A_1 is its amplitude, and θ_2 and A_2 the corresponding quantities for b, then one has

$$\theta_1 = A_1 \cos \omega t \text{ and } \theta_2 = A_2 (\cos \omega t - \Psi) \quad \text{----(1)}$$

where $\omega = 2\pi f$ is the angular frequency. The angle θ at the cross-over point is then determined by the relations:

$$\theta = A_1 \cos \omega t_c = A_2 \cos (\omega t_c - \Psi) \quad \text{----(2)}$$

where t_c is the time at which the crossing occurs. Since $\frac{\theta}{A_1}$ and $\frac{\theta}{A_2}$ are in general small, one can use for convenience developments in series and one obtains in first approximation:

$$\Psi = \frac{\theta}{A_2} \left\{ 1 - \frac{A_2}{A_1} \right\} \quad \text{----(3)}$$

In a typical example the following values were recorded:

$\theta = 2.0, 5.7, 2.9$; $A_1 = 49.7, 53.1, 49.6$; and $A_2 = 47.9, 47.7, 27.7$ at 26°C , 0°C and -40°C respectively. The errors in Ψ due to neglecting higher order terms are 6%, 13 and 3%.

However, the error in reading the various quantities on the scale is $\pm .1$ which yields an error for the single reading of about 4% at -40°C where the loss peak occurs in this case.

At higher temperatures due to the decrease of the elastic modulus of the samples, A_2 becomes nearly equal to A_1 and the method just discussed becomes unprecise. Under these conditions another procedure is followed: the angle θ is measured at that time when $\theta_1 = 0$ and $\Psi = \frac{\theta_2}{A_2}$, using again the first approximation only. This method was used, for example, in the case of polyvinyl acetate which has a transition temperature near 35°C and has a low modulus. The maximum value of $\frac{\theta}{A_2}$ was

0.09 while λ_2 expressed as distance on the scale was about 33 cm. For recording when $\theta_1 = 0$ it is necessary to follow the two spots simultaneously, which is not as convenient as the observation of the cross-over points, and thus the latter method was always preferred when the conditions permitted it.

The phase angle Ψ as determined by the two methods just mentioned can now be related to the anelastic constants of the sample. Let G_1 be the complex shear modulus of the copper wire and α_1 a constant depending on its geometrical dimensions, and similarly G_2 and α_2 the corresponding quantities for the sample. Then, as long as the frequency of the torsional oscillations ω is much lower than the resonance frequency of the sample-wire system (which is greater than 100 cps), one has

$$\alpha_2 G_2 \theta_2 = \alpha_1 G_1 (\theta_1 - \theta_2) \quad \dots(4)$$

and since G_1 and G_2 are both complex

$$\alpha_2 (G_2' + iG_2'') \theta_2 = \alpha_1 (G_1' + iG_1'') (\theta_1 - \theta_2) \quad \dots(5)$$

Writing θ_1 and θ_2 as $A_1 e^{i\omega t}$ and $A_2 e^{i(\omega t - \Psi)}$ respectively, one obtains:

$$\{\alpha_2 (G_2' + iG_2'') + \alpha_1 (G_1' + iG_1'')\} A_2 e^{i\Psi} = \alpha_1 (G_1' + iG_1'') A_1 \quad \dots(6)$$

from which G_2' and G_2'' can be calculated

$$G_2' = \frac{\alpha_1}{\alpha_2} \frac{G_1' (A_1 \cos \Psi - A_2) + G_1'' (A_1 \sin \Psi)}{A_2} \quad \dots(7)$$

and

$$G_2'' = \frac{\alpha_1}{\alpha_2} \frac{G_1'' (A_1 \cos \Psi - A_2) - G_1' (A_1 \sin \Psi)}{A_2} \quad \dots(8)$$

Because Ψ is small-- the highest values observed were about

.15--one can again use a first approximation and write:

$$G_2' = \frac{\alpha_1}{\alpha_2} G_1' \left\{ \left(\frac{A_1}{A_2} - 1 \right) - \frac{G_1''}{G_1'} \frac{A_1}{A_2} \Psi \right\} \quad \dots(9)$$

and

$$G_2'' = \frac{\alpha_1}{\alpha_2} G_1' \left\{ \frac{G_1''}{G_1'} \left(\frac{A_1}{A_2} - 1 \right) - \frac{A_1}{A_2} \Psi \right\} \quad \dots(10)$$

-14-

The value of the factor $\frac{G_2''}{G_1'}$ is of the order of 3×10^{-3} as determined experimentally by replacing the polymer sample by a copper wire similar to the one used as suspension. This value includes the losses due to the clamping. The largest value of ψ as mentioned above was 0.15, the values of $\frac{A_1}{A_2}$ are of the order of 2 to 3. The last term in the bracket in equation 9 is of the order of 10^{-3} while the first term is of the order of 1. In most cases the last term can, therefore, be neglected.

In equation 10 the first term in the bracket has a value of the order of 3×10^{-3} near the transition region while the second term is of the order of 2×10^{-1} . Thus the first term is about $\frac{1}{100}$ th of the second. Neglecting this term is therefore also justified. In the auxiliary experiment using a copper wire in place of the sample it was found that the damping due to the wire and the clamping was nearly constant throughout the whole temperature range and, therefore, though the first term affects the absolute values of G_2'' it does not change the position of the peak as a function of temperature, the study of which is the prime objective of this work. The absolute values are also influenced by the inherent uncertainty in the values of C_1' and C_2' . These errors were caused by unevenness of the dimensions of the samples, uneven clamping and some stretching during the experiment.

A schematic diagram of the apparatus used for this type of measurement is shown in figure 2, and a photograph of the equipment is given in figure 1. In its latest design it could operate at the frequencies 5.8×10^{-2} , 1.5×10^{-2} , 3.6×10^{-3} ,

and 9.0×10^{-4} cycles per second. The sinusoidally varying torque was applied by means of a cam-operated mechanism. The rate of oscillations could be changed to any of the four values by shifting gears in the drive mechanism, while the amplitude of the applied torque could be varied by repositioning an adjustable pivot. Motor and gears were outside a can which contained the sample. The motion so generated was transferred through a magnetic coupling to a carriage supported on jewel bearings inside the can. This provided a very simple means of transmitting the torque, eliminating the need for a moveable vacuum joint. However, because of the lack of rigid coupling, the amplitude A_1 varied somewhat due to the variations in the elastic properties of the sample as the temperature changed, even though the amplitude of the motion of the magnet was kept constant. The cell was evacuated by means of a fore-pump during the experiment in order to avoid condensation of the moisture in and around the sample. As already mentioned by Woods, the presence of moisture in the sample can shift the position of the loss peak, in a similar way as is observed with the addition of a plasticizer.

A copper wire of 3.54×10^{-2} cm diameter could be screwed to the lower end of the carriage. The lower end of the wire was soldered to a thin stainless steel tube which had a brass clamp b at the other end. This brass clamp secured the other end of the polymer sample in form of a strip of about $5 \times 1 \times 0.03$ cms. The lower end of the sample was held fixed in a base clamp at the bottom of a double walled cylinder which served as a cooling or heating jacket. This clamp did not

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permit any rotation of the lower end of the sample about its vertical axis but permitted, by means of two springs, some compensation of uneven stretching along its two vertical edges. The copper wire was stretched straight pulling the sample upright and was then screwed to the carriage. The jacket was held in position with two stainless steel pipes which served as inlet and outlet for liquid nitrogen for cooling or for hot air for heating. It was possible to make measurements down to -185°C and up to $+45^{\circ}\text{C}$. For heating to still higher temperatures, up to about 90°C , infrared lamps were employed to heat the whole cell from outside and air was let into the cell to improve the heat transfer to the sample. The temperature could be maintained to better than a degree for a period of one minute except below -140°C where the rise in temperature was somewhat faster. For the very low frequencies where the period was of the order of minutes, the temperature changed slightly during the time needed for the measurement, and the temperature was read before and after each measurement, and an average was taken. The temperatures were measured by means of two copper-constantan thermocouples, one placed near one end, and the other near the middle of the sample. An average of the two readings was taken.

Two mirrors were mounted on the carriage and on the upper clamp of the sample, and two spots of lights were reflected onto a curved scale of radius of curvature 183 cms and placed at about 180 cm from the mirrors. The positions of the two spots were adjusted to coincide when the sample was unstrained. The spot from the lower mirror was very sensitive to outside vibrations. Foam rubber cushions were

put under the three legs of the angle iron stand which supported the cell. In turn, the wooden board which supported the stand rested on compressed rubber shock absorbers.

During the cooling and heating some samples twisted, probably due to internal stresses introduced during the preparation of the sheets of materials from which the samples were cut. This shifted the center position of the light beams and made its readjustment necessary as the temperature changed. Measurements were more reproducible when the sample was warming up after being cooled down to the lowest desirable temperature, though some runs were made during cooling also, in order to check if there was any hysteresis. If the rate of cooling was slow enough, no such effect was found.

The geometrical constants α_1 , and α_2 were computed according to

$$\alpha_1 = \frac{\pi R^4}{2 l_w} \quad \dots(11)$$

and

$$\alpha_2 = \frac{wt^3}{6I_2} \left(1 - \frac{6t}{w}\right) \quad \dots(12)$$

where R is the radius of the wire and l_w its length, and w , t and l_2 are the width, thickness and length of the sample respectively.

b. The Medium Frequency Region.

For frequencies of approximately one cycle per second, the decay of the amplitude of oscillations of a freely vibrating torsion pendulum was measured. The pendulum consisted of a copper wire and a narrow strip of the polymer sample in series as shown in figure 4. The upper end of the copper wire and the lower end of the polymer sample were clamped rigidly to the support system. An inertia member was mounted at the place

where the wire was attached to the polymer sample. This member was rotated slightly about the vertical axis twisting the wire and the sample, and was then released, setting the pendulum into a damped free rotary oscillation. As long as the damping is not too high, one can write the equations of motion using again complex moduli:

$$I \ddot{\theta} = -(\alpha_1 G_1 \theta + \alpha_2 G_2 \theta) \quad \dots (13)$$

α_1 , G_1 and α_2 , G_2 refer to the same quantities as in the case a. I is the moment of inertia of the pendulum bob and θ the angle of torsion. Setting

$$\theta = \theta_0 e^{i\omega t} = \theta_0 e^{i\omega(1 - \frac{\delta}{2\pi})t} \quad \dots (14)$$

one obtains

$$G_1' = \frac{4\pi^2 I f^2}{\alpha_2} - \frac{I \delta^2 f^2}{\alpha_2} - \frac{\alpha_1}{\alpha_2} G_1' \quad \dots (15)$$

and

$$G_2'' = 4\pi I \delta f^2 - \frac{\alpha_1}{\alpha_2} G_1'' \quad \dots (16)$$

The maximum value of δ ever recorded in these experiments was less than 0.3. Therefore, δ^2 was about 10^{-1} and the maximum values of f^2 were about 10 for $I = 81$ gm. cm^2 , and about 1 for $I = 1300$ gm. cm^2 . Therefore, in equation 15 the second term on the right side is about 400 times smaller than the first term, and can thus be neglected. In equation 16, however, the second term on the right hand side is not negligible especially when δ is small. However, G_1'' as mentioned earlier varies only little with temperature. This term, therefore, though changing the absolute value of G_2'' does not affect the position of the transition peak. This term has been neglected in the computations merely for sake of convenience.

The logarithmic decrement is determined by observing the amplitudes of oscillation: δ is given by $\frac{1}{n} \log \frac{A_1}{A_{n+1}}$ where

A_1 is the amplitude of the first and A_{n+1} that of the $(n+1)$ th oscillation. Knowing I , G_1 , and G_2 from geometrical dimensions and obtaining δ and f^2 from the experiment, G_2' and G_2'' can be computed.

It should be mentioned here that the formulae developed above are valid only if the system can be considered as one of one degree of freedom, i.e., if the frequency of the pendulum is very low as compared to the resonance frequencies of the torsional vibrations of the wire and the sample alone. This condition was always fulfilled in these experiments.

The same enclosure was used as in method a, see figure 1. The forced torsion arrangement was replaced by the torsion pendulum assembly. For this purpose the upper carriage with jewel bearings was replaced by a fixed clamp to which the upper end of the copper wire was attached by means of a screw at a. The lower end of the copper wire was soldered to a thin stainless steel tube which carried a clamp b at its lower end, and the upper end of the sample was clamped at b while its lower end was secured in the base clamp at the bottom of the cooling jacket in the same manner as in method a. During mounting of the sample the upper end of the wire was stretched a little and then screwed tight. A horizontal flat iron bar, welded at its center to the stainless steel tube and carrying at its two ends two brass cups, formed the inertial member. The cups could be filled with lead shots or interchanged with heavier blocks to provide different moments of inertia and, therefore, different periods of oscillation.

Directly underneath the pendulum bar an electro-magnet was placed such that its pole pieces were displaced by about 10 degrees with respect to the axis of the bar when the latter was at its rest position.

The whole assembly was enclosed in an outer jacket not shown in the figures 2 and 4 but visible in the photograph figure 1. The enclosure is covered with a layer of asbestos to reduce heat conduction, and was evacuated so that besides removing moisture from the cell and the sample it also reduced damping due to air friction to a negligible amount.

The electromagnet was energized by means of a relay for a short period only, so as to impart an impulse to the pendulum. If the field were left on for a longer period, additional damping would be created by the motion of the bar in the magnetic field. Since the impulse was of the same magnitude every time, it started oscillations of almost the same initial amplitude for one set of readings at each temperature.

A small mirror mounted on the tube above the bar reflected a spot of light onto a scale just as in method a.

Up to twenty oscillations were timed to obtain the frequency. The amplitudes before and after any n oscillations were noted and δ computed from these readings. Cooling or heating and recording of temperatures was just as in method a. Values of I were calculated from the weight of each member of the pendulum and its geometric dimensions.

c. The High Frequency System.

Most of the measurements at frequencies greater than 1 cps were made by Woods¹²; however, subsequent to his work, his equipment was modified slightly and a few additional

measurements made.

Woods also measured the decay of the amplitude of vibration of a freely oscillating body, but in his case the oscillations were the transverse flexure of a reed and the system was not loaded with a mass. Since some of the samples were very flexible and not stiff enough to keep themselves in a fixed position or to support a drive coil, and since damping took such high values, that the vibration of the sample alone would have been nearly aperiodic, a composite oscillator was used. A brass strip was clamped at one end and the sample was attached to it at the other end. The metal was excited into transverse vibration and its decay was measured. By adjusting the ratio of the masses of the metal reed and that of the specimen, a damping of the composite oscillator could be obtained that was in the optimum frequency range. Since the polymer sample influences only to a small degree the resonance frequency f_0 but essentially determines its damping δ , it was found that f_0 varies only little with temperature. As a consequence δ of the whole system and G_2'' of the sample are proportional, with a proportionality constant which is practically constant for a complete temperature run.

To excite the vibration a small coil of about 100 turns of no. 42 A.W.G. and weighing about 3 gm. was attached to the end of the metal reed in the case of the composite oscillator, or at the end of the plastic sample in those cases where it was stiff enough to support the coil (e.g. pure cellulose nitrate). The samples were of the order of $3 \times \frac{3}{4}$ cm. cut from the same sheets as the samples used in methods a and b. The coil lay between the pole-pieces of a loudspeaker type

permanent magnet, (see figure 5) a signal fed into the coil from an audio oscillator was tuned to the resonance frequency of the system. The oscillator output level could be regulated so as to keep the amplitude at a desirable value. By means of two relays the input signal was then cut off and the coil leads were immediately connected through an amplifier to a counter with discrimination which was so adjusted that the counting stopped when the amplitude was below $\frac{1}{2}$ of the original value. These functions are shown in figure 6. The reciprocal of the number of counts registered by the counter gave the value for δ . The signal could also be viewed on an oscilloscope. A band pass filter was inserted in the circuit in order to cut down the noise and outside pick up.

The sample and the magnet were covered with a double walled jacket (see figure 5) which could be cooled by pumping liquid nitrogen through it as in previous methods or heated by means of heating coils. The temperatures were measured by two thermocouples mounted on a dummy sample clamped parallel to the sample under investigation. The cell was evacuated. For every value of the temperature an average of at least five counts of n was taken.

The variations in the counts of n were caused to a large part by the slight variations in the making and breaking of the relays. To avoid this cause of error, the method was somewhat changed. A tiny permanent magnet was attached to the sample on the opposite side of the coil and displaced from the axis of the coil. The magnet moved inside another coil of a great number of turns and connected to the scope and the counter through the same amplifying circuit. With this arrangement the relays were eliminated.

The main difficulty with this system was the fact that the composite oscillator could vibrate in more than one mode, unless the brass reed and the specimen were completely matched. Since the elastic properties of the sample changed markedly with temperature, the composite oscillator also changed its mode of vibration giving rise to peaks that were difficult to interpret quantitatively.

Various other modifications were tried, such as clamping the sample on both ends, taking resonance curves instead of decay times, and others, but in general the results were not entirely satisfactory. It became clear that for these samples, with their very special properties, it would be necessary to develop a new method. However, since time was lacking to undertake new developments, and since the results are believed to be of general interest, if not entirely quantitatively satisfactory, they are included in this report.

B. Dielectric Measurements.

If the sample forms part of the dielectric medium of a condenser, the imaginary part of the complex dielectric constant, ϵ'' , can be determined from $\frac{1}{R\omega} = G/\omega = \epsilon'' C_0$ where C_0 is the capacity of the condenser in vacuum, R is the resistance, G the conductance, and ω the angular frequency of the applied electric field. With a conventional bridge circuit, Woods measured G/ω and capacity C of polymer samples over a temperature range of -180°C to $+150^\circ\text{C}$ and for frequencies of 30, 152, 552, 5520 cps. Since C_0 is a constant independent of temperature, the behavior of ϵ'' with temperature can be described by plotting G/ω versus $t^\circ\text{C}$ curves.

In the present work, the measuring cell used was the

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same as that of Woods with slight modifications with respect to the method of controlling temperature. The cell, illustrated in Fig. 7, could be evacuated; cooling was done with liquid Nitrogen, and heating by Michroms coils. The samples were in the form of circular disks, previously described, sandwiched between two carefully surfaced brass disks. For frequencies from 60 cps to 50 kc a resistance capacitance a.c. bridge (General Radio 716-c Bridge) was used. For frequencies above 50 kc a Q-meter (Boonton Radio Corp. Type 160A) was used. This instrument reads directly the Q value of the system and from this the Q/ω was computed. Samples were studied from frequencies from 60 cps to 2 mcps at temperatures from -170°C to $+70^{\circ}\text{C}$ approximately.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Introduction. It is accepted that both electrical and mechanical losses obey relaxation laws and can be represented in good approximation by the form

$$\frac{\omega\tau}{1+\omega\tau}$$

or by a sum of such terms with different relaxation times, τ . In the studies reported herein, the main interest was given to T_{max} , the temperature at which, for a given frequency, ω , the losses show a maximum. For this temperature, $\omega\tau = 1$, and thus one obtains a value for τ and its variation with temperature.

Relaxation phenomena are often explained by a rate process expressed as an exponential temperature dependence, of the form:

$$\tau = \tau_0 e^{E/KT}$$

where E is the activation energy of the molecular process.

The validity of this concept can be tested by plotting $\ln.f$ vs. $1/T$ where $T = T_{max}$ for the frequency at which the loss is measured: $\tau = 1/\omega$ at T_{max} .

If the relation above is correct, $\ln.f$ vs. $1/T_{max}$ should be a straight line independent of how many relaxation frequencies have to be assumed to represent the loss curves, provided all relaxation frequencies are related to a single activation energy. Ferry¹⁵ has shown this to be true for the substances studied in this investigation. Therefore T_{max} will be used for the study of the temperature dependence of the losses.

Part 1. Polyvinyl Acetate.

Both mechanical and electrical loss measurements were made on this material, mostly by one individual^(ref. 12) in the Laboratory, but some measurements were repeated by a second investigator later with modified equipment^(ref. 14) and were extended to lower frequencies. The mechanical loss measurements shown in figure 8 were taken with the vibrating reed system; those shown in figure 9 and 10 with the torsion pendulum. The latter figure illustrates one of the problems in making these measurements,-- the effect of adsorption of water vapor from the atmosphere. Measurements taken with carefully dried air gave the same results as for the vacuum case.

As seen in figures 8 and 9 the temperature dependence of the frequency has an inflection at about the same temperature as that of the maximum loss. In figure 8 the dashed curve was run one day later than the others, as a check on the reproducibility of the measurements. Marked "plastic" flow of the sample began at about 75°C and hence limited the mechanical loss observations to temperatures below this value.

To explore further the effect of room air, the electrical loss of polyvinyl acetate was measured (by the method shown in figure 7) at four widely separated frequencies in room air and in vacuum. In figure 11 the peaks only of the loss curves are shown and the effect of moisture adsorption is clearly seen. Since water is plasticizer for some polymers, and plasticizers lower the transition temperature, the effect is not unexpected. No shift in loss peak was found for dry air so care was taken to keep the samples in dry air.

Electrical losses σ/ω and dielectric constant ϵ' vs. temperature are shown in figure 12. The symmetry of these curves lends strength to the electrical loss theory with only one relaxation constant τ . In the Cole-Cole¹⁶ plot of this data, figure 13, ϵ'' vs. ϵ' at 63°C, the angle $\theta = \alpha \pi/2$ is a measure of how closely the losses approach those for a single relaxation time for which $\alpha = 0$. In this data, $\alpha = 0.1$. There is also evidence that the real part of the dielectric constant (ϵ') has an inflection point at T_{max} (see figure 12) as predicted.

Both mechanical and electrical loss measurements were taken over a wide temperature range (-160° to +20°C) with constant (but different) frequency. A not very sharp peak, see figure 15, exists for the electrical loss but only an inflection was found in the mechanical losses. The marked increase in loss beginning about -40°C is the tail of the loss curve observed at higher temperatures and is believed to be due to a different loss mechanism than that of the peak in figure 15. Also the absolute value of the peak in figure 15 is an order of magnitude lower than the "higher temperature" peak, and the activation energy is much lower.

$\ln f$ (where $f = \omega/2\pi$) vs. $1/T_{max}$ is shown in figure 14 for both types of measurements. The first work was done by Woods¹² and extended by Vardhan¹⁴, who carried (with modified equipment) the mechanical observations down to 2.3×10^{-4} cps. Woods' data (upper part of graph) gives an activation energy of 57 KCal/mole which is in good agreement with the value of 59 reported by Meeds and Fuoss²⁰.

In extending the measurements to 2.3×10^{-4} cps the technique of recording ϵ_2 when $\epsilon_1 = 0$ was used and the position of the loss peak with temperature studied as the sample was warmed and cooled. A difference of about 1°C in the position was found.

That the activation energy is not constant but changes for lower frequencies is definitely established by Vardhan's measurements. If one interprets the curve as two separate straight lines as is indicated in the figure⁽¹⁴⁾, a value of 120 KCal. results for the low frequency portion. The reciprocal of the transition temperature (30°C) as determined by Kokes and Long¹⁷ from diffusion measurements is 3.3×10^{-3} , the last scale division shown in figure 14. All the loss peaks observed, even at the lowest frequencies, are still at higher temperatures than the transition temperature, and one is tempted to speculate that the transition temperature is the limit to which the peak would move if the frequency approaches zero.

Part 2. Cellulose Acetate.

Mechanical loss measurements were made by Woods¹² on pure 2.3 acetate only. Electrical losses and dielectric constant were measured by both Woods and Vardhan¹⁴ for pure 2.3 acetate, and by Vardhan only for cellulose 2.3 acetate with 50% K-17 santicizer, cellulose triacetate and cellulose triacetate plasticized with 50% metacresol. All the observations were made over the temperature range -160°C to $+150^\circ\text{C}$.

The electrical losses Q/ω vs. temperature at four frequencies for pure cellulose acetate are shown in figure 16. These peaks are broad and not symmetrical; the inflection point of the real part of the dielectric constant curve is not clearly present and does not correspond well with the maximum of the loss curve. It is believed that these low temperature losses have a different mechanism than those found at high temperatures in polyvinyl acetate.

For pure cellulose triacetate, the loss Q/ω vs. temperature are shown in figure 17. At the lower three frequencies two peaks are apparent. The peak appearing at temperatures from -65°C to $+45^{\circ}\text{C}$ gives an activation energy of 9.5 KCal/mole. Only four points are available from which to compute the activation energy for the second peak, hence the value of 43 KCal/mole so determined may be in considerable error. At the higher temperatures the softening of the material introduces a very large background. Four samples were studied; figure 17 shows the results taken with one sample. The curves for the other three samples are similar in appearance except that they show only one set of peaks, and that the peaks occur at different temperatures resulting in different values of activation energy.

Figure 18 presents the $\ln f$ vs. $1/T_{\text{max}}$ relation for four materials; the activation energy for each is listed. There are two lines for the pure cellulose 2.3 acetate; the one from 50 kc upwards results from Vardhan's measurements whereas the one from 50 kc downward to 50 cps are from Woods' data taken from two different sets of experiments.

Although parallel, the shift of Vardhan's data towards higher temperatures can perhaps be explained on the basis of solvent content in the samples. Woods' measurements were made shortly after the samples had been prepared, and it is not excluded that traces of solvent were present which disappeared during the interval of several months between his and Vardhan's measurements, during which time the sample was in a dry place and sometimes even in vacuum. The presence of solvent like that of moisture makes the peak appear at lower temperatures.

For this same substance Woods made some mechanical measurements which are included in *Fig. 18*; the values agree well with the dielectric measurements.

When cellulose 2,3 acetate is plasticized with 50% M-17, the peaks occur at -7°C to $+43^{\circ}\text{C}$ for 300 cps to 105 kc giving an activation energy of 35 KCal/mole. In figure 18 the results of three sets of measurements are reproduced. The points of each set fall on different lines but the slope of all three lines is the same. The three different experiments were performed at three different times and the shifts are believed to be due to a gradual evaporation of moisture or, more probably, of the plasticizer. In fact, the later measurements which would have less plasticizer according to this interpretation, gave the lines at the higher temperatures.

Cellulose triacetate with 50% metacresol showed peaks at -25°C to -10°C giving 45 KCal/mole activation energy. This value is nearly the same as that calculated from the second set of peaks observed in pure triacetate at higher temperatures, as mentioned earlier. The two sets of peaks

in pure triacetate giving different activation energies are evidently the result of two different processes. Addition of the plasticizer shifts both peaks to lower temperatures. On this basis, for 63 cps the peak at about 100°C has shifted to about -35°C on addition of 50% metacresol. If we assume at least the same amount of shift for the lower peak, occurring at -60°C in pure triacetate, it may be expected that ^{with} the addition of the metacresol it has shifted to temperatures outside the range covered by the equipment.

Similarly the activation energy of 35 KCal/mole for the santicized 2.3 acetate corresponds to a process which, in pure cellulose 2.3 acetate, would occur at higher temperatures. However, no such peak was observed at the temperatures where the peak would be expected to occur. It is not clear what causes the difference between the tri- and the 2.3 acetates. The two samples were prepared by different experimenters and the amount of crystallinity, and possibly traces of solvent, may account for this discrepancy.

The same of activation energy, namely 9.5 KCal/mole for both the 2.3 acetate and the triacetate leads one to conclude that this is independent of the degree of "acetation." On the other hand, there is a difference of about 10 KCal. in the activation energies for the two plasticized samples. How significant the 10 KCal. difference is, seems difficult to decide. It is well possible that it is due to the different chemical character of the plasticizer; indeed, a similar difference has been observed in cellulose nitrate (see later).

Of the two plasticizers, M-17, with the higher boiling point, gives the lower activation energy. It may also be noted that the curve with higher activation energy is shifted towards lower temperature, in opposition to the general rule that relaxation processes occurring at lower temperatures have also lower activation energies. Apart from this, M-17 and meta-cresol give very similar results, though according to Russell and Van Kerpel¹⁸ the meta-cresol freezes at +8°C. It thus appears that the action of the plasticizer is not dependent on the state in which it is present in the sample.

Nakamura¹⁹ concluded that the transition shifts to lower temperature and the activation energy decreases with increasing acetyl content. However, from figure 18, for the two pure acetates it is found that corresponding transitions for the triacetate occur at higher temperatures, which is contrary to Nakamura's observation. Also that the activation energy is not less for the triacetate than that for 2.3 acetate as should be according to his view. Mead and Fuoss²⁰ found that the transitions for polyvinyl acetate-gelva 60, which was heavier and more viscous than polyvinyl acetate-gelva 15, occurred at higher temperatures than those for gelva 15. This is in line with the result of figure 13.

Mandlekern and Flory²¹ have reported two transitions for the 2.3 acetate at 60°C and 120°C and two for the triacetate at 30°C and 105°C as obtained from volumetric measurements. Russell and Van Kerpel¹⁸ have found in similar experiments two transitions for the 2.3 acetate at 55°C and 115°C and three for the triacetate at 40°C, 120°C and 155°C.

The differences in the positions of the corresponding transitions found by Mandlekern and Flory and by Russell and Van Kerpel are small and could be due to slight differences in the materials used. However, since the volumetric measurements can be considered "zero frequency" measurements, these transition temperatures should be the lower limit of any set of peaks which might be found by the method of the present investigation. Therefore, the transition of Mandlekern and Flory at 30°C and that of Russell and Van Kerpel at 40°C for the triacetate corresponds in the present case to the high temperature set of peaks with an activation energy of about 43 KCal/mole. To the low temperature peaks observed in the present study would correspond a volumetric transition temperature of -100°C or lower, which has not yet been observed. The advantage of loss measurements to detect transitions is here evident. On the other hand, this method is unsuccessful at higher temperatures because of the onset of flow.

For cellulose 2,3 acetate with M-17 Russell and Van Kerpel¹⁸ report three transitions at nearly 30°C, 70°C and 100°C and, for cellulose triacetate with metacresol, two transitions at 70°C and 99°C. If addition of 50% metacresol shifts the transition by 135 degrees as discussed before, it is hard to say which of these above-mentioned transitions correspond to which of those of the pure samples.

Russell and Van Kerpel also performed some mechanical measurements (torsion pendulum, approximately 1 cps)--and this is the reason such measurements were not made in the

present study--on the same samples and found correlation with some of the peaks but not with all the transitions observed by the dilatrometric method.

A typical mechanical loss measurement made by Woods on pure cellulose acetate is shown in Fig. 19. The line labeled background in the figure is the loss measured without the sample attached to the reed and coil (see page 21). The results of a number of curves taken at different frequencies are included in Fig. 18. The results of the mechanical and electrical measurements agree very well.

Part 3. Nitrocellulose.

a. Pure and Plasticized but Uncross-linked.

Pure: Both mechanical and dielectric losses for nitrocellulose samples were observed over the temperature range of approximately -180°C to $+60^{\circ}\text{C}$. In the dielectric measurements the transition peaks were in many cases rather flat and a precise determination of the transition temperatures for different frequencies is not possible. The mechanical measurements resulted in satisfactorily sharp peaks.

A number of samples of the pure material were studied by both Woods and Vardhan, but each investigator used samples prepared at different times. Typical results are shown in Figs. 20 and 22 for electrical and mechanical losses, respectively, by Woods¹²; and in Figs. 21 and 27, respectively, by Vardhan.¹⁴ Activation energies were computed from the lines drawn in Fig. 23 for Woods' data and from Fig. 28 for Vardhan's data. Woods' value of the activation energy, 4.6 KCal/mole,

is considerably lower than the values of 10 to 18 KCal/mole calculated from the later measurements. No explanation, other than the difference in preparation of the samples, is apparent.

The results on cellulose nitrate, Fig. 28, give two, non-colinear lines, as was found for polyvinyl acetate, Fig. 14.

Only one measurement with the vibrating reed method was made. This value, for 150 cps vibration, is plotted on Fig. 28 and agrees well with other measurements.

Plasticity When the nitrate was plasticized with 4.8% diethyl phthalate evidence of the presence of peaks in the G/ω versus $t^{\circ}\text{C}$ curves became still fainter; but increasing the plasticizer content to 16.8% the occurrence of peaks becomes somewhat more pronounced; see Fig. 24. In this case, the curves of 63 cps and 115 cps showed two flat peaks at about -45°C and $+15^{\circ}\text{C}$. The peaks, however, seem to fade away with increase in frequency. It is still not possible to obtain a value of activation energy from these curves.

With higher plasticizer content, 41.4%, 49.9% and 60.7% diethyl phthalate (DEP) the G/ω versus $t^{\circ}\text{C}$ curves show quite pronounced peaks, but only one set of peaks for each. These occur at 12°C to 42°C , 12°C to 37°C and 5°C to 29°C for frequencies of 60 cps to 50 kc for the three samples respectively. As an example, the measurements on the 49.9% sample are reduced in Fig. 25. The activation energies calculated from these peaks are 41.6, 43.8, and 47.6 KCal/mole. The $\log f$ versus $1/T_{\text{max}}$ lines for these and for pure cellulose nitrate are shown in Fig. 26.

Mechanical losses also were measured for samples containing 4.8%, 16.7%, 41.6%, 49.9%, and 60.7% DEP plasticizer. Typical results for the 4.8% and 16.7% are illustrated by the results shown in Fig. 29 for the 16.7% samples. Both cases show double peaks, with a possible third peak faintly seen for the 4.8% sample. Activation energies of 23 and 41 KCal/mole were found for the two peaks and 39 and 53 KCal/mole likewise in the 4.8% and 16.7% samples respectively. When the DEP (plasticizer) content is increased to 41.1% the Q_2'' curves show only single peaks around about -41°C with an activation energy of 50 KCal/mole. These seem, therefore, to correspond to the third peaks mentioned above, but shifted to lower temperatures due to increased plasticization. These curves along with Q_2' plots are shown in Fig. 30.

Measurements on the samples containing 49.9% and 60.7% DEP show single peaks but shifted still further towards lower temperatures. The results of mechanical measurements versus plasticizer content may be summarized as follows:

Cellulose Nitrate

Plasticizer % DEP	Peaks	Activation Energy K-Cal/mole	
		Mechanical	Electrical
0	1--sharp	18	10
4.8	2 + 1 uncertain	23, 41	—
16.7	2 definite	39, 53	—
41.6	only 1--sharp	50	42
49.9	single	46	44
60.7	single	48	48

A picture of what happens when a plasticizer is added in increasing amounts is seen in Fig. 31. which shows the G_2'' curves for all plasticizer contents used, at one frequency $--3.62 \times 10^{-3}$ cps. The pronounced shift of the corresponding peaks is large at first as the plasticizer content is changed, being about 1.6 degrees per 1% change in the plasticizer for peak III from 16.7% to 41.4%. However, this shift becomes relatively smaller when the plasticizer changed from 41.4% to 49.9%, being about 0.57 degree per 1% plasticizer again for peak III. It becomes 0.12 degree per 1% plasticizer change in the 49.9% to 60.7% range. It seems, therefore, that the effectiveness of the plasticizer decreases as its fraction in the polymer increases. The dependence of T_{max} on plasticizer concentration at constant temperature is very similar to the variation of the transition temperature as determined by Uberreiter¹⁰ from volumetric measurements. As Boyer and Spencer⁸ pointed out this dependence agrees only in a limited range of concentration with a formula they derived from earlier work of Flory²², according to which

$$W_2^{1/2} = A - B/T$$

where W_2 is the weight fraction of the Polymer, T the absolute temperature and A and B are constants (for a specific system). The deviations at high concentration, where T_{max} changes much less than indicated by this formula, may not be too surprising. At these high concentrations the segments of the polymer molecules whose motion is responsible for the losses in this frequency and temperature region, are already surrounded by

the plasticizer molecules. This surrounding determines the effective viscosity, and, since further addition of plasticizer will not change this surrounding, and thus the viscosity significantly, the T_{max} should not change.

b. Plasticized and Stabilized.

Since most of the plasticized samples showed aging effects that were interpreted as changes in the plasticizer content, it seemed of interest to study a sample containing a stabilizer. In fact, the measurements were better reproducible, even over long time intervals.

Two samples, one plasticized with 50% di(2-ethyl hexyl) phthalate (DOP)--which is considered as a more stable plasticizer--and the other plasticized with 49% DOP and stabilized with 1% stabilizer were investigated for both the dielectric and the elastic behavior.

The G/ω versus temperature curves for the unstabilized sample showed peaks in the range from -10°C to $+37^{\circ}\text{C}$ for frequencies of 150 cps to 50 kc, giving 29 KCal/mole for the activation energy. It may be recalled from the previous section that similar curves for the sample with 49.9% DEP had peaks between $+15^{\circ}\text{C}$ and $+39^{\circ}\text{C}$ for the same frequencies, giving about 43 KCal/mole for the activation energy. It seems, therefore, that the chemical structure of a plasticizer exercises a definite influence on the value of the activation energy.

From the mechanical measurements on this sample an activation energy of 41 KCal/mole can be calculated with

the transitions occurring in the region of -50°C to -20°C . This region corresponds to the region of the transition peaks of the electrical measurements which were at higher frequencies. Therefore, the loss peaks observed in the mechanical and electrical measurements seem to originate from the same process. The difference of about 10 KCal/mole between the activation energy observed from the mechanical and dielectric measurements is thus similar to that found with polyvinyl acetate. The value of the activation energy for 41 KCal/mole is also quite close to the 46 KCal/mole obtained for the sample with 49.9% DEP. It thus appears that the different chemical constitution of the plasticizer is not so effective in this case as it is in the dielectric measurements. The heights of the G_2'' curves, for both the 50% DOP and the 49.5% DEP samples are nearly the same. The modulus G_2' however, is somewhat less for the sample containing DOP.

For the sample plasticized with 49% DOP and stabilized with 1% stabilizer, the G/ω curves, Fig. 32, give transition peaks from -15°C to $+31^{\circ}\text{C}$ for frequencies from 115 cps to 50 kc leading to 19 KCal/mole for the activation energy. This is about 10 KCal/mole less than that for the sample without the stabilizer discussed above. Also, the peaks are not as well-defined and pronounced in this case.

The activation energy calculated from the mechanical measurements is about 20 KCal/mole, —higher by about the same amount than the dielectric value as in the unstabilized sample. This regularity of the behavior seems to indicate

that the presence of the stabilizer reduces the activation energy both in the dielectric and the mechanical behavior.

c. Plasticized and Cross-linked.

Four samples of cellulose nitrate plasticized with 50% DEP and cross-linked to various degrees were studied with respect to dielectric as well as mechanical losses.

The G/ω versus temperature curves from the dielectric measurements at frequencies from 115 cps to 5 kc showed peaks in the region from -19°C to $+10^{\circ}\text{C}$, -15°C to $+10^{\circ}\text{C}$, -15°C to $+14^{\circ}\text{C}$ and -15°C to $+13^{\circ}\text{C}$, giving activation energies of 30, 30, 34.5 and 36.2 KCal/mole for the samples containing 2.44%, 1.44%, 0.74% and 0.74% of cross-linking agent HDI and with cross-linking of $q_m = 0.70, 0.62, 0.18$, and 0.06 respectively. Figs. 33 and 34 show a set of such curves for the least cross-linked sample obtained with the bridge and the Q-meter respectively. $\log f$ vs. $1/T_{\text{max}}$ plotted for the peaks of these figures gives an activation energy of 30 KCal/mole. The high frequency measurements up to about 2 mc were taken for the other three samples also. Fig. 35 lists the activation energies for all the four cross-linked samples. A plot for the uncross-linked sample with 49.9% DEP is also reproduced for comparison. A definite change of the activation energy in the four samples is noted although it is not very large (30-36 KCal/mole). For the two samples containing 0.74% HDI but having different degrees of cross-linking $q_m = 0.18$ and 0.06 , the variation of the activation energy is rather related to the HDI content and not to the degree of cross-linking, since both give the same value for activation energy, namely, 30 KCal/mole, so,

with increasing degree of cross-linking, the corresponding transitions occur at somewhat lower temperatures. The cross-linking, on the other hand, has reduced the activation energy by about 10 KCal/mole from that of the uncross-linked sample. It is interesting to recall that the presence of 1% of a stabilizer in a 49% plasticized sample also reduced the activation energy by almost the same amount. Physically, therefore, the stabilizer and the cross-linking agent seem to act in a similar manner.

For the anelastic response, the activation energy for all the four samples has a constant value of 44 KCal/mole as shown in Fig. 37. The corresponding G_2'' peaks occur at lower temperatures for samples with greater cross-linking. This shift in the positions of the peaks is more pronounced for the mechanical measurements than for the electrical ones. This shift is in an opposite direction to what one would expect. In fact, cross-linking produces a more rigid material, and the transition should shift to higher temperatures, as is observed, for example, for rubber of different degrees of vulcanization.^{7d}

The constant value of activation energy for the four samples obtained from mechanical measurements is larger than the values calculated on the basis of dielectric measurements by an amount of the same order of magnitude--i.e., about 10 KCal/mole--as for the pure cellulose nitrate or for the samples plasticized with 50% DOP and plasticized with 49% DOP and stabilize.

It may also be noted that the activation energy from mechanical measurements for the cross-linked samples does not differ from the corresponding activation energy (46 KCal/m.) for the uncross-linked sample. This behavior is different from that found for the stabilized and unstabilized samples. Thus, as far as the anelastic behavior is concerned, cross-linking and stabilization do not seem to have similar effects.

For sake of illustration, a curve of G_2'' versus temperature from pendulum measurements is shown, Fig. 36, for the least cross-linked sample. Though the plots of G_2'' and G_2' for the four samples do not represent the absolute values with great precision, as stated before, they give definite indications that G_2'' and especially G_2' are constant for all the four samples. This is again contrary to expectation because cross-linking is expected to increase the modulus.

Reviewing the results obtained with cross-linked samples, one gains the impression that there is no very marked influence. It may well be that the observed differences in the dielectric or anelastic behavior are due rather to differences in preparation and life history of the samples than to the effect of cross-linking. It may also be pointed out that Aldrich²³ found in the case of hevea that cross-linking did not influence the viscoelastic observation; however, he worked in the ultrasonic range, and a direct comparison may not be valid.

V. CONCLUSIONS

In this investigation emphasis was put upon finding the location of the loss peaks on the temperature scale and investigating their shifts with frequency, plasticizer and cross-linking, etc. No effort was therefore made to compare the complete curves over the whole temperature range. By using several frequencies, activation energies could be computed from curves representing $\log f$ versus $1/T_{max}$.

Since the location of the peak on the temperature scale is dependent on the preparation of the test specimen and since there are often several peaks, the corresponding peaks occurring at different frequencies could be distinguished by their activation energy.

It is found that the activation energy is not constant with temperature but increases as the static transition temperature is approached. Examples are polyvinyl acetate, pure cellulose nitrate and some of the plasticized samples.

No basic distinction could be found in the dielectric behavior of cellulose triacetate and cellulose 2.3 acetate.

It can be concluded that the addition of a plasticizer does not change radically the value of the activation energy for any particular transition but only shifts it to lower temperatures. This shift becomes relatively smaller as the plasticizer content increases.

The addition of a stabilizer makes the measurements more consistent and reproducible. Its presence reduces the activation energy in a way very similar to that of a cross-linking agent.

Contrary to expectation, cross-linking reduces the value of the activation energy for the dielectric measurements. Its presence did not make any appreciable difference for the mechanical measurements. However, in both cases, the transitions shift to lower temperatures.

Plasticized samples are found to be rather unstable. It is suspected that the plasticizer evaporates during the experiment, thus often leading to incorrect results. This erratic behavior renders it difficult to make precise statements.

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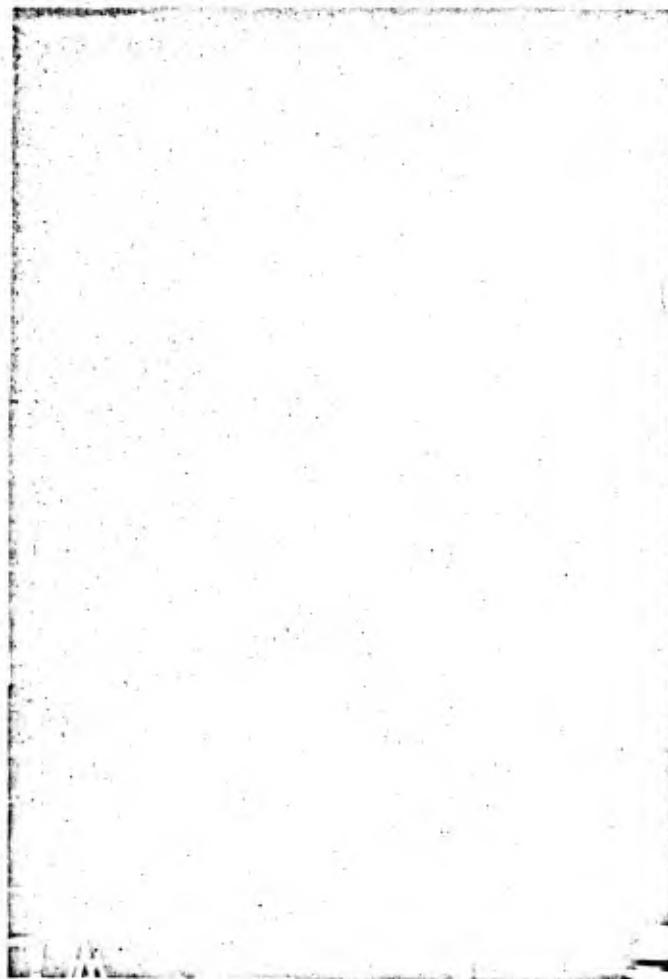
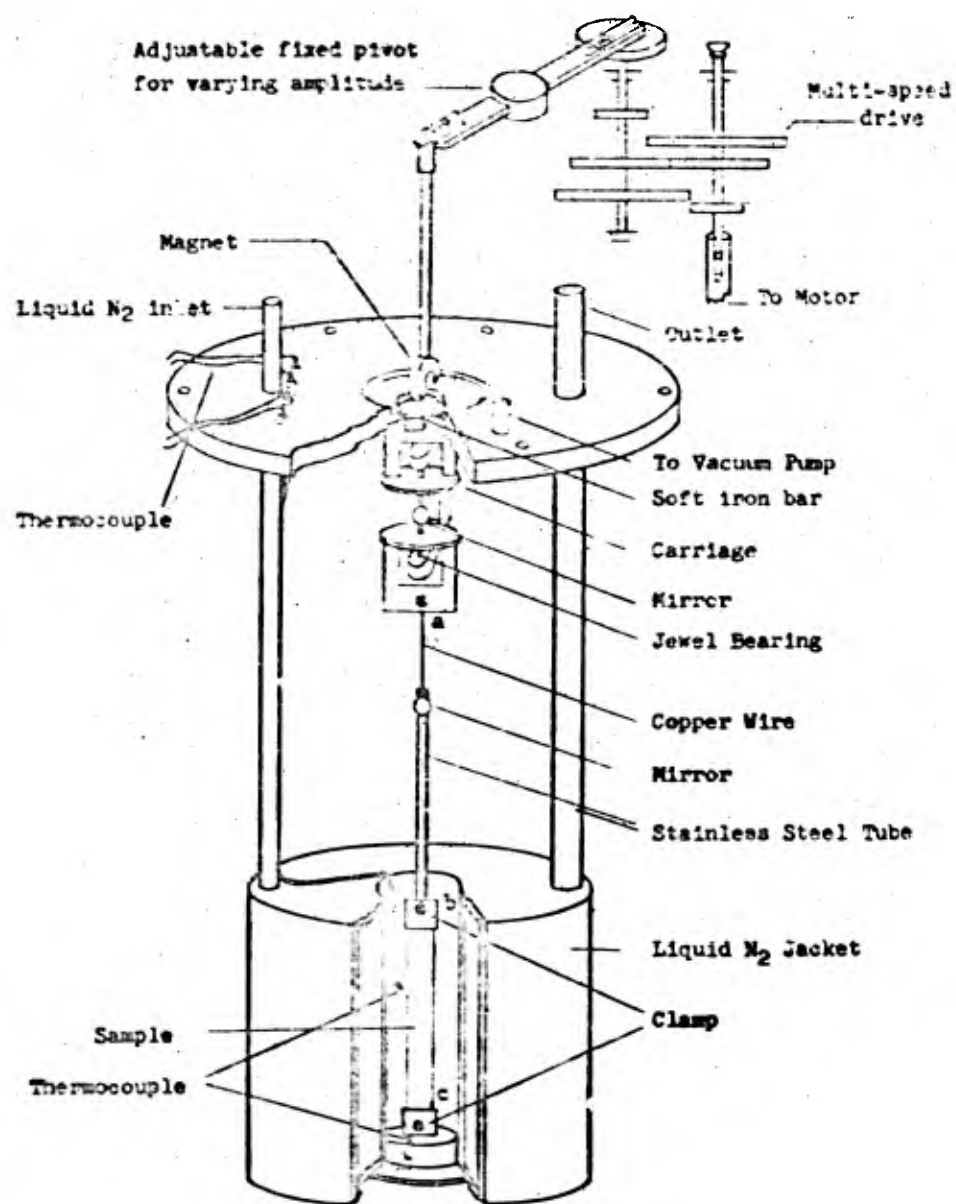


Figure 1.



Schematic diagram of Torsion Method

Figure 2

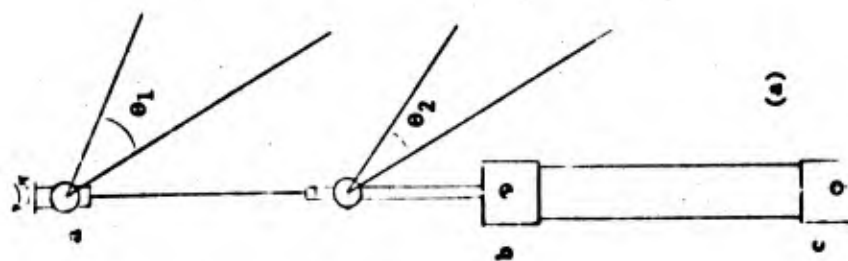
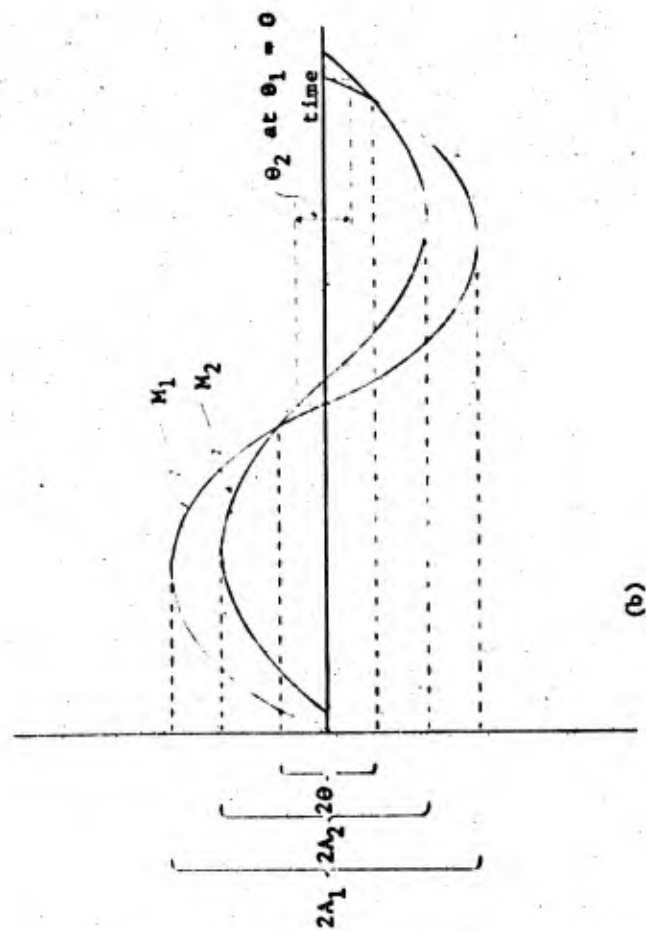
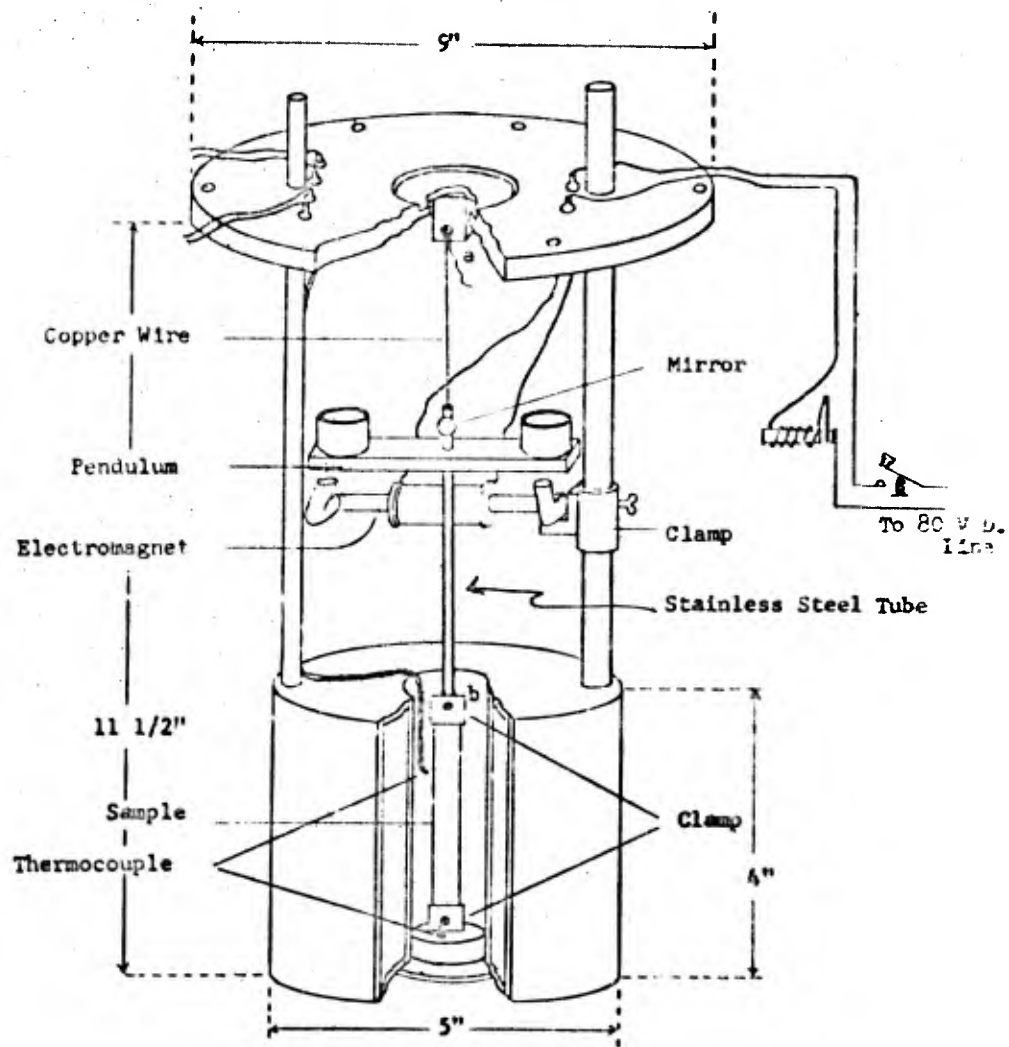


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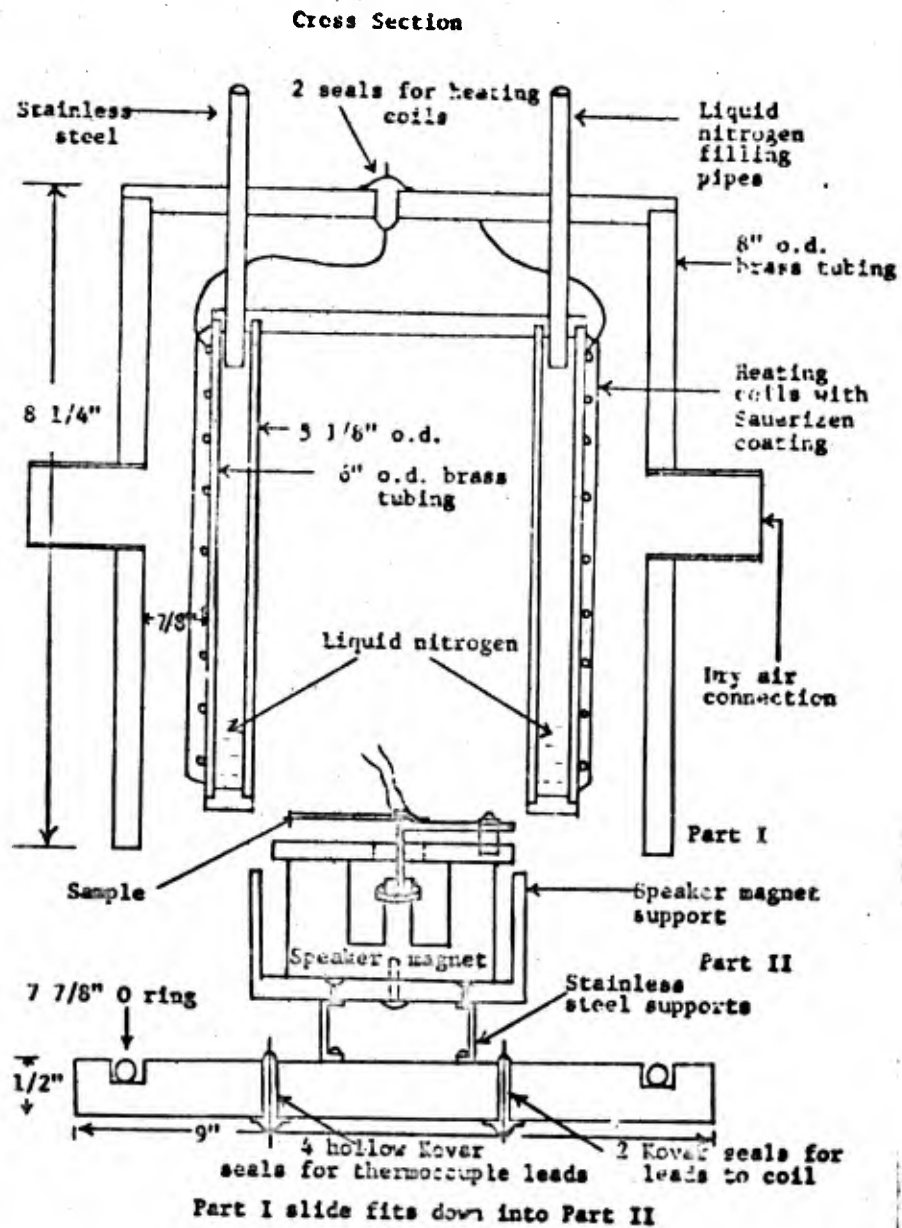


Principle of Torsion Method



Schematic Diagram of Pendulum Method

Figure 4



Design of Vibrating Reed Cell

Figure 5

BLOCK DIAGRAM OF DRIVE AND PICK UP OF VIBRATING REED SYSTEM

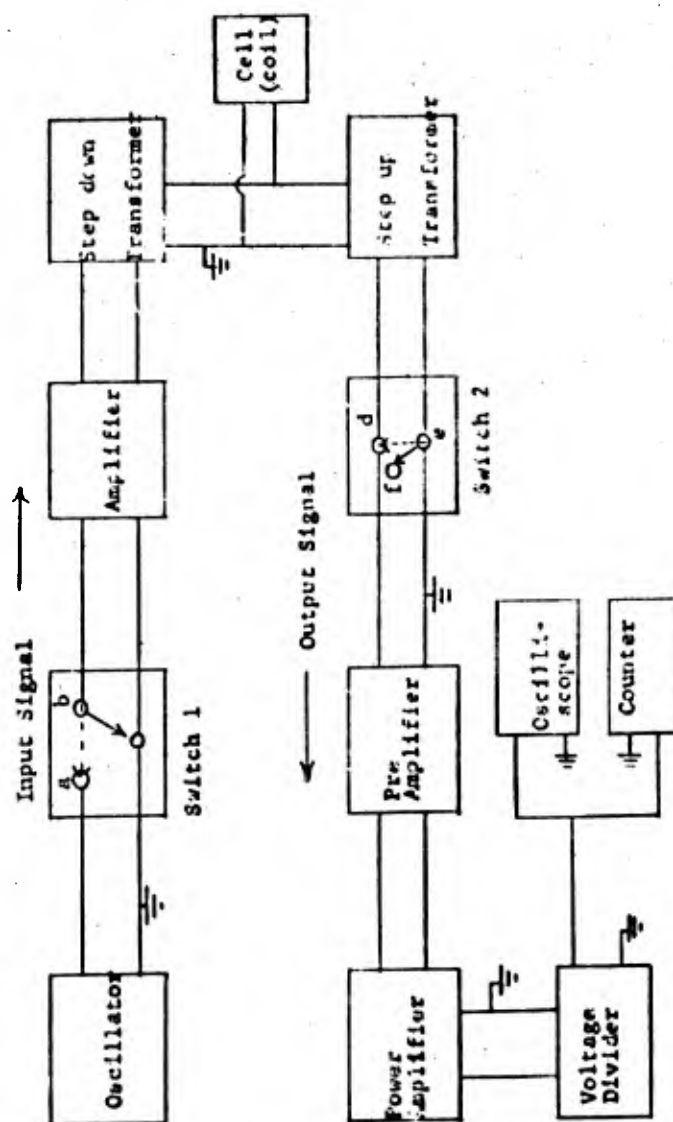
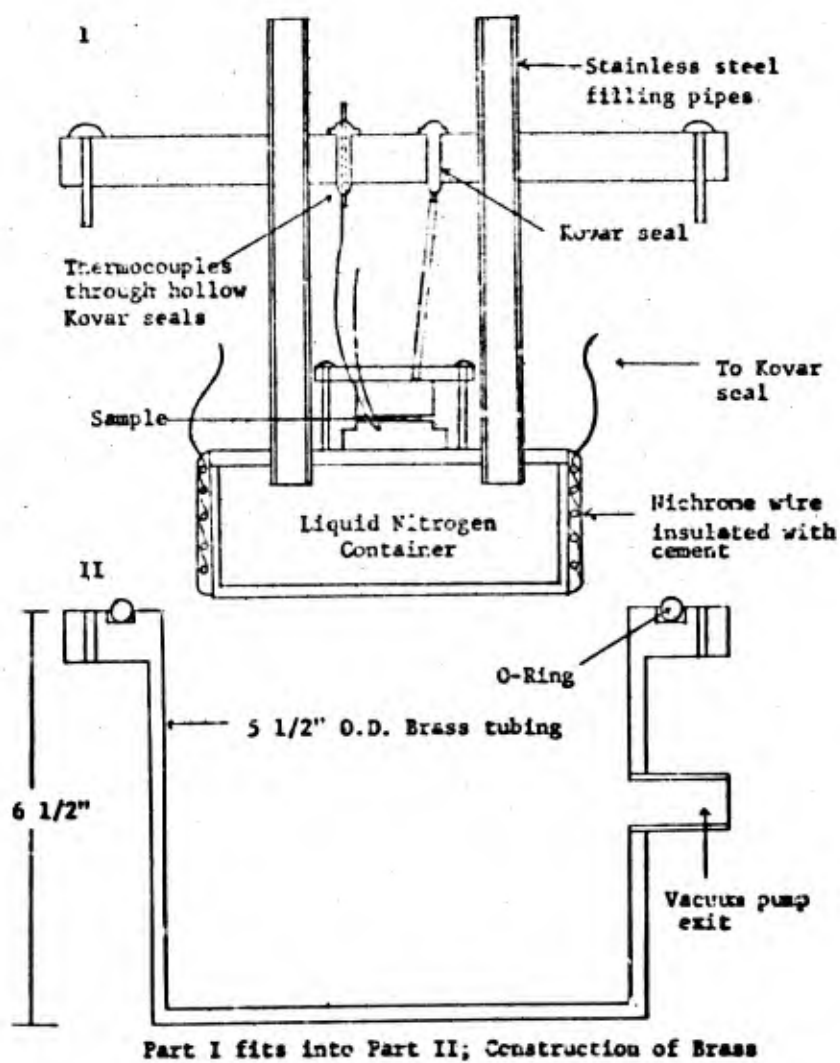


Figure 6

Vertical cross section through center axis



ELECTRICAL MEASUREMENT CELL

Figure 7

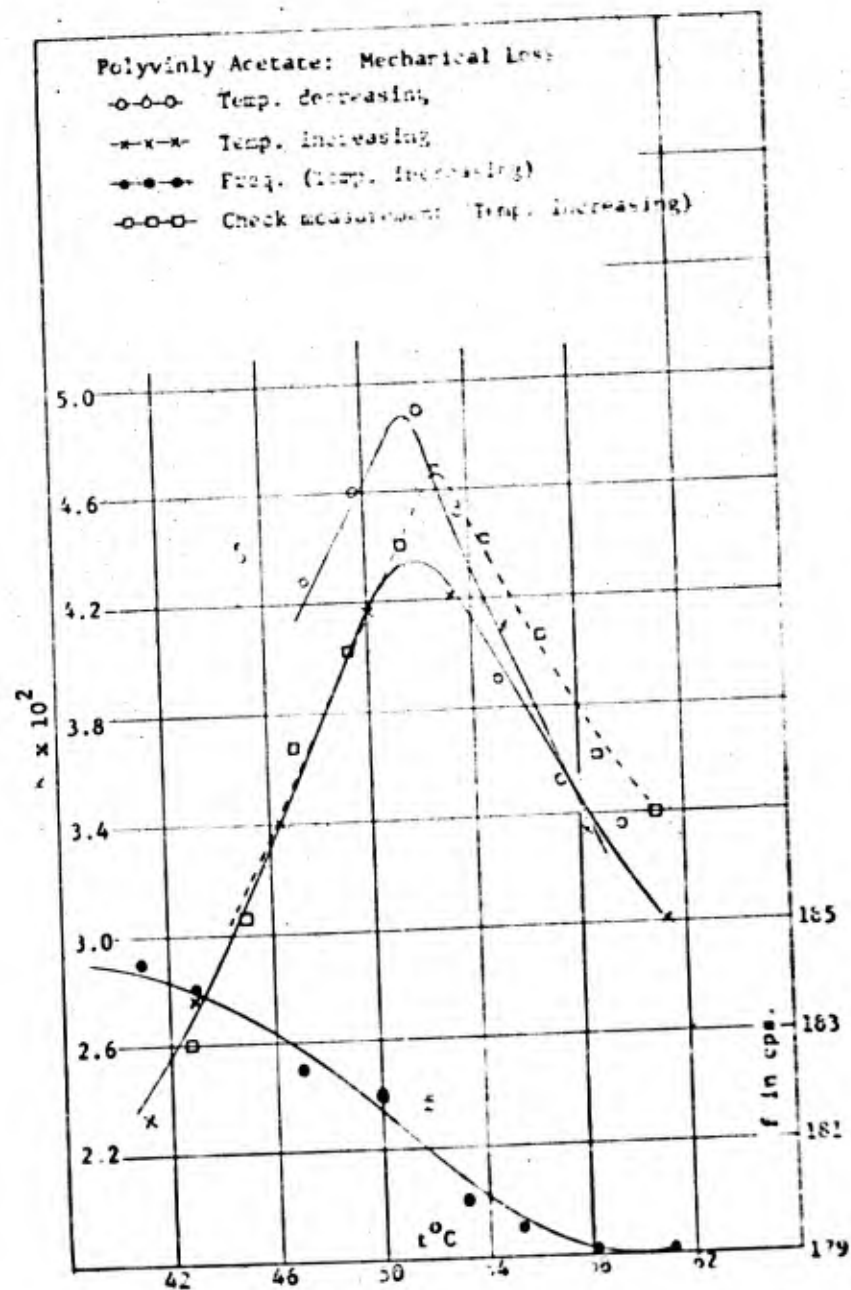


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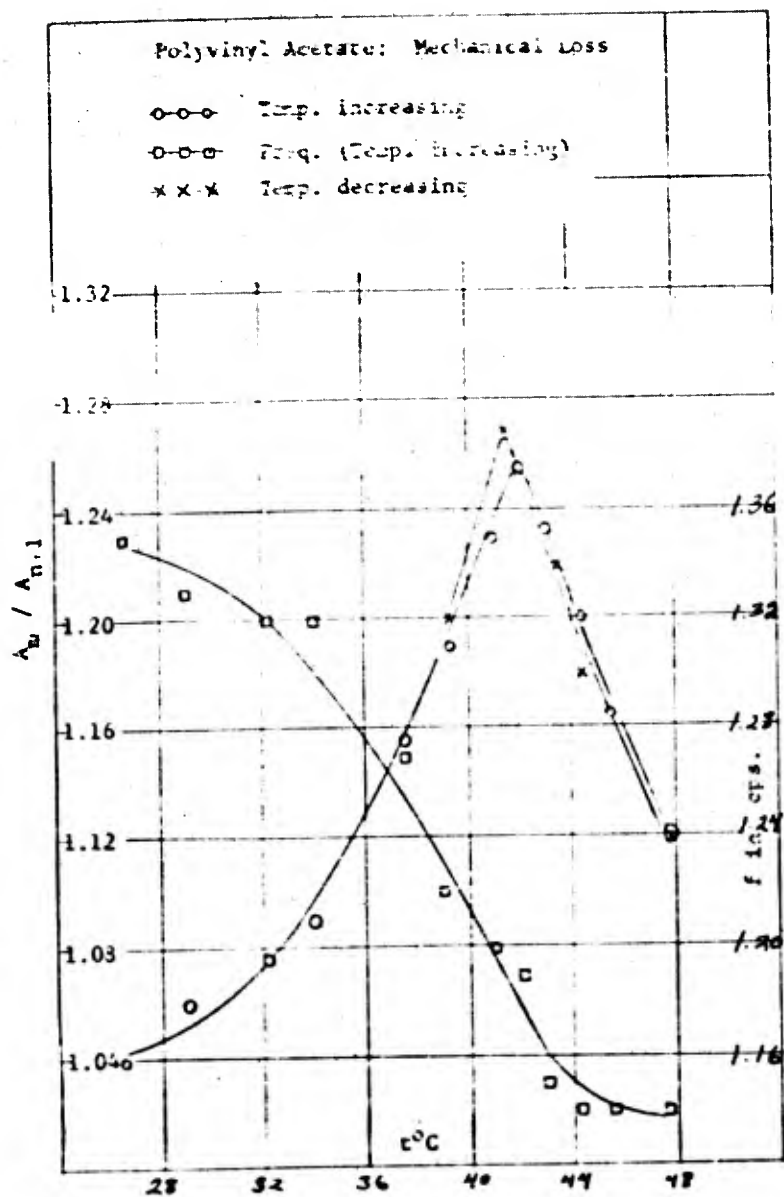


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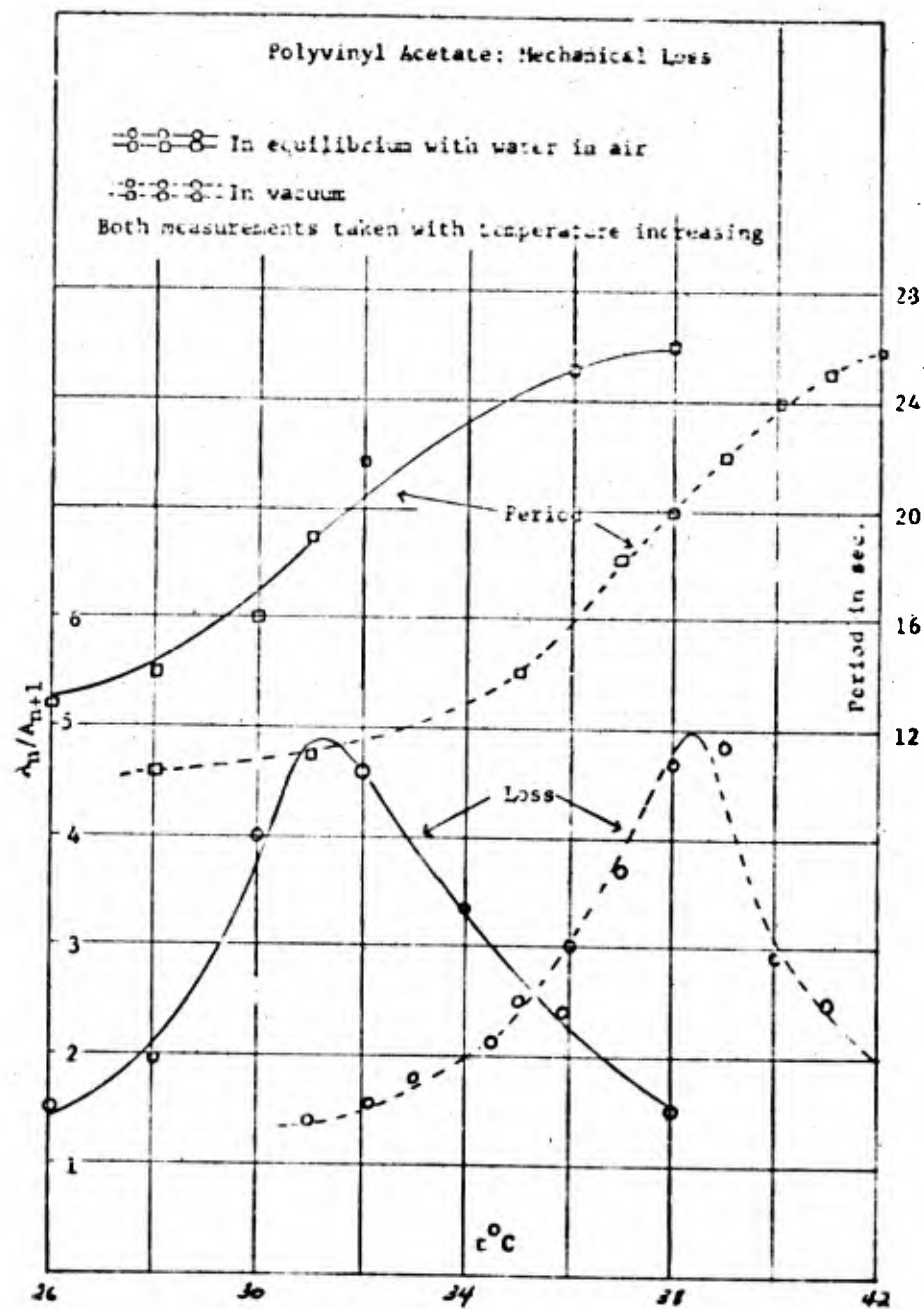


Figure 10

Polyvinyl Acetate: Electrical Loss

Showing Temperature Shift due to Absorption of water vapour

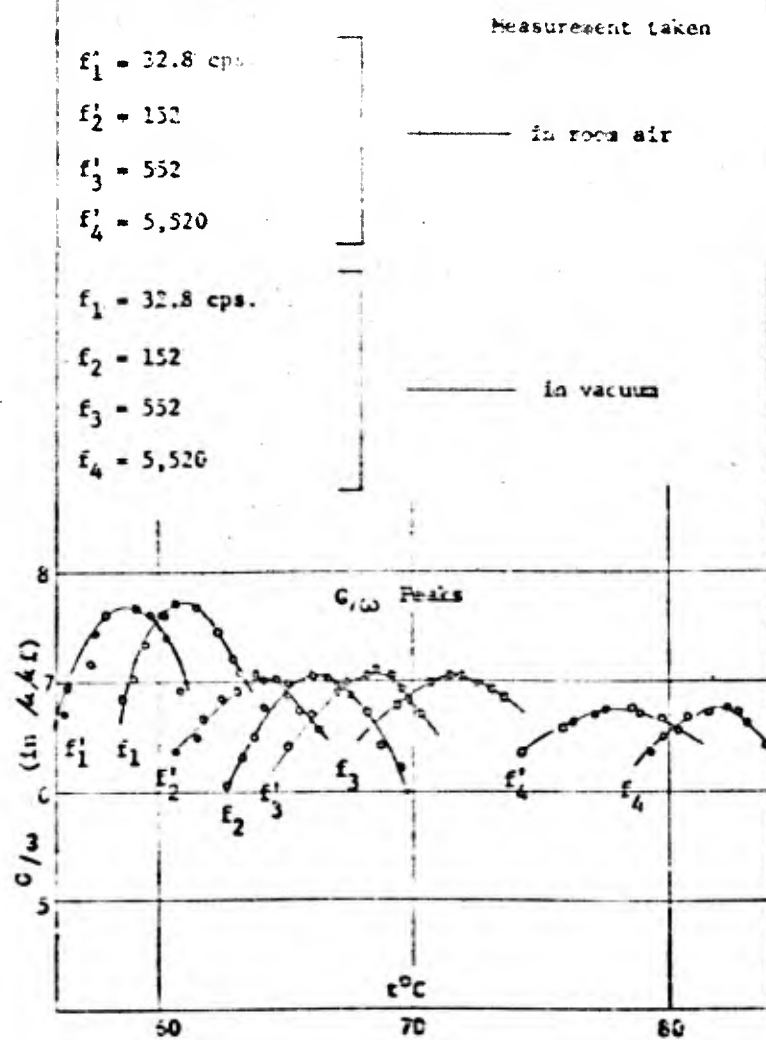


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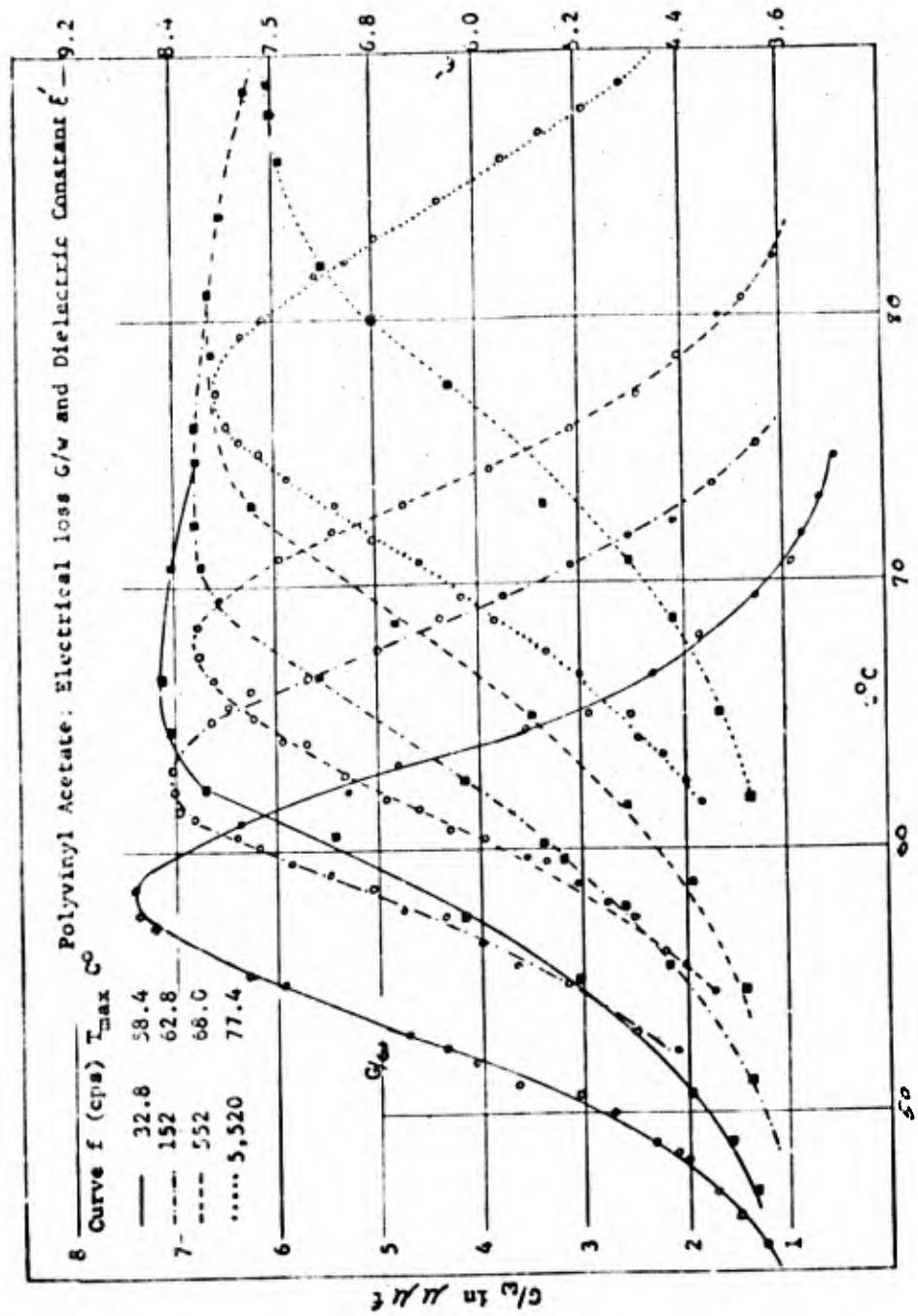


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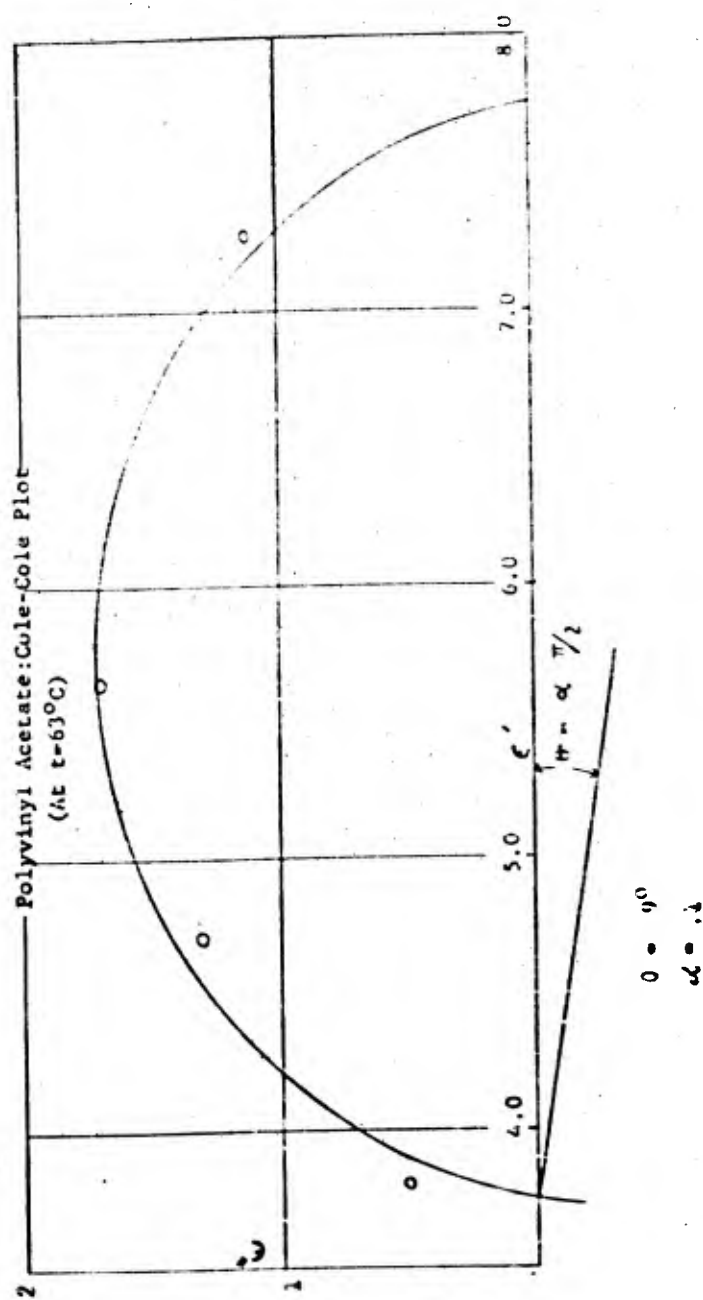


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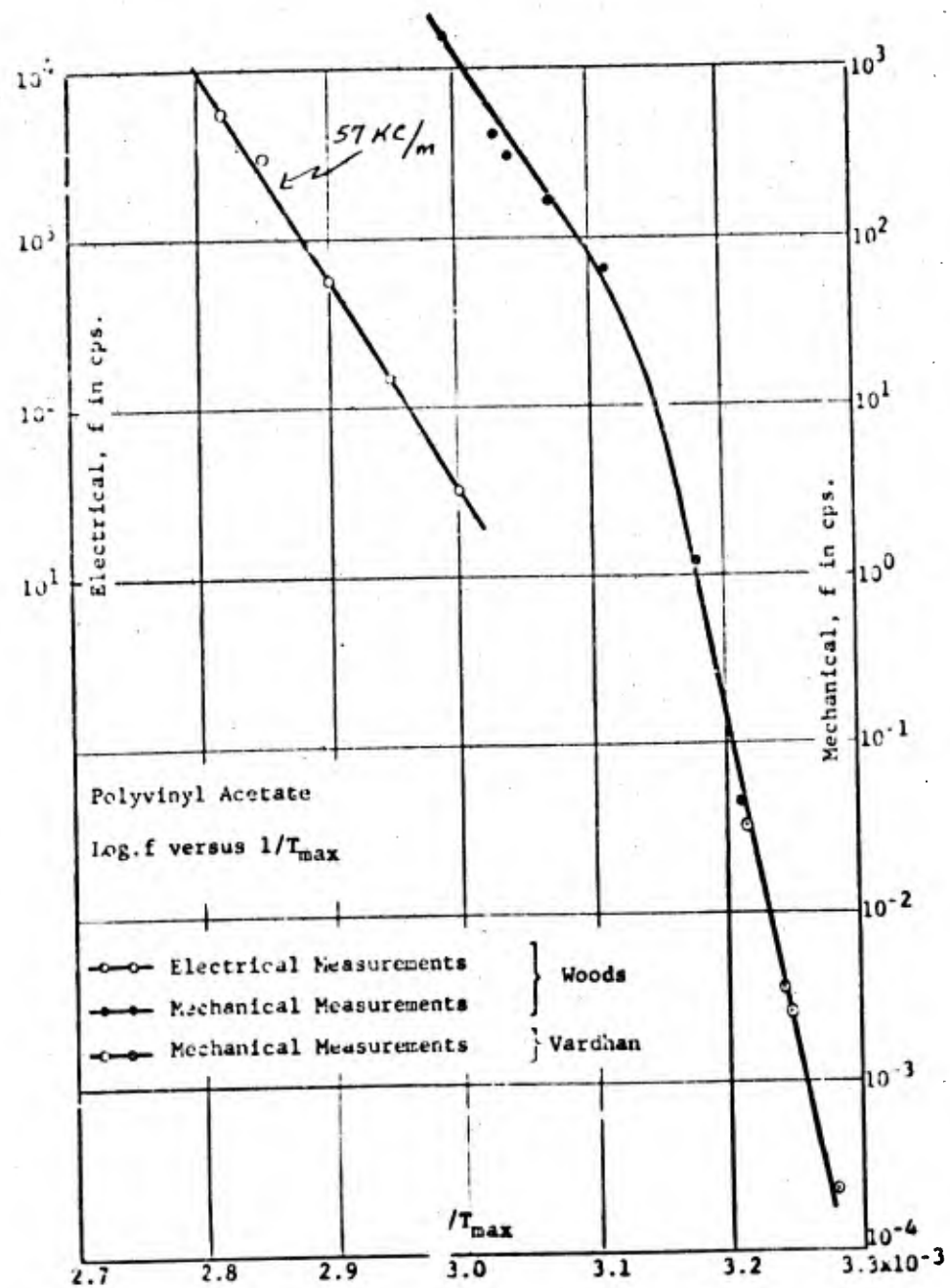


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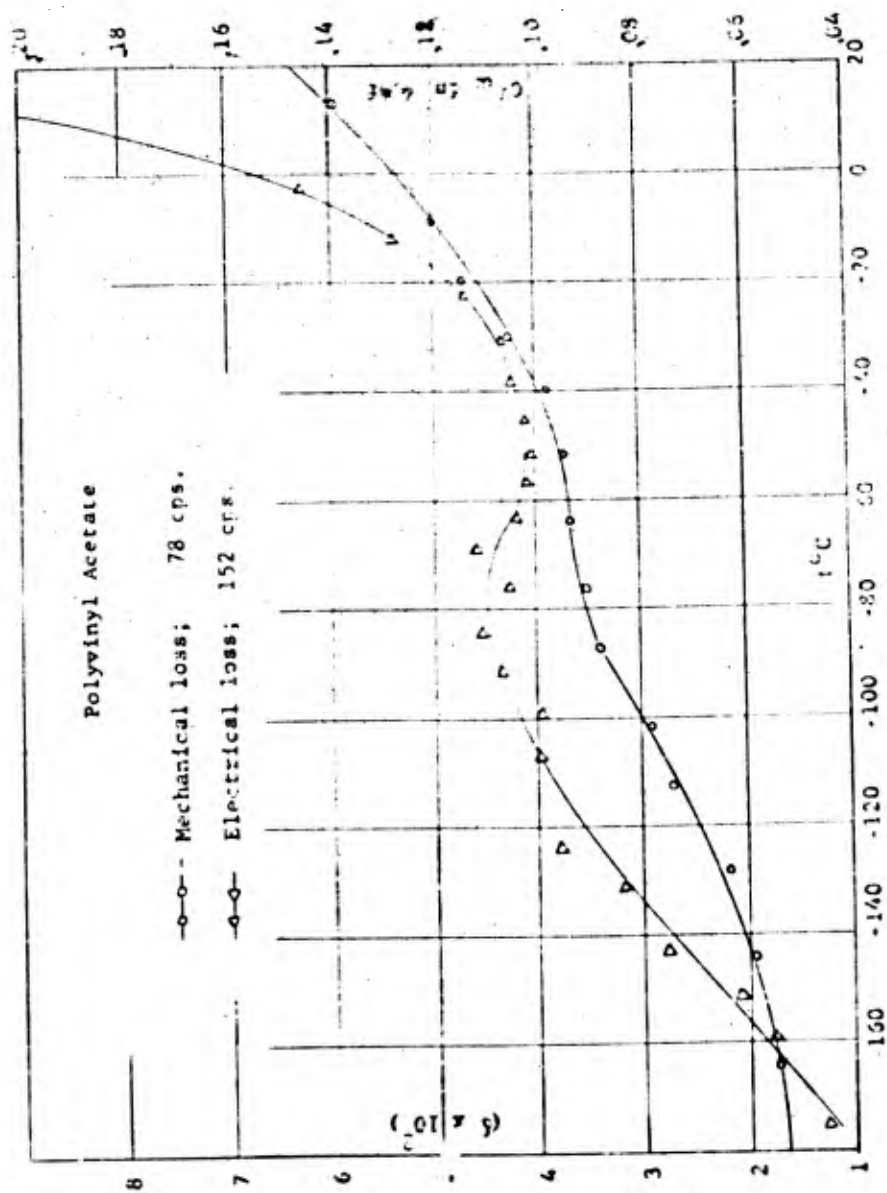


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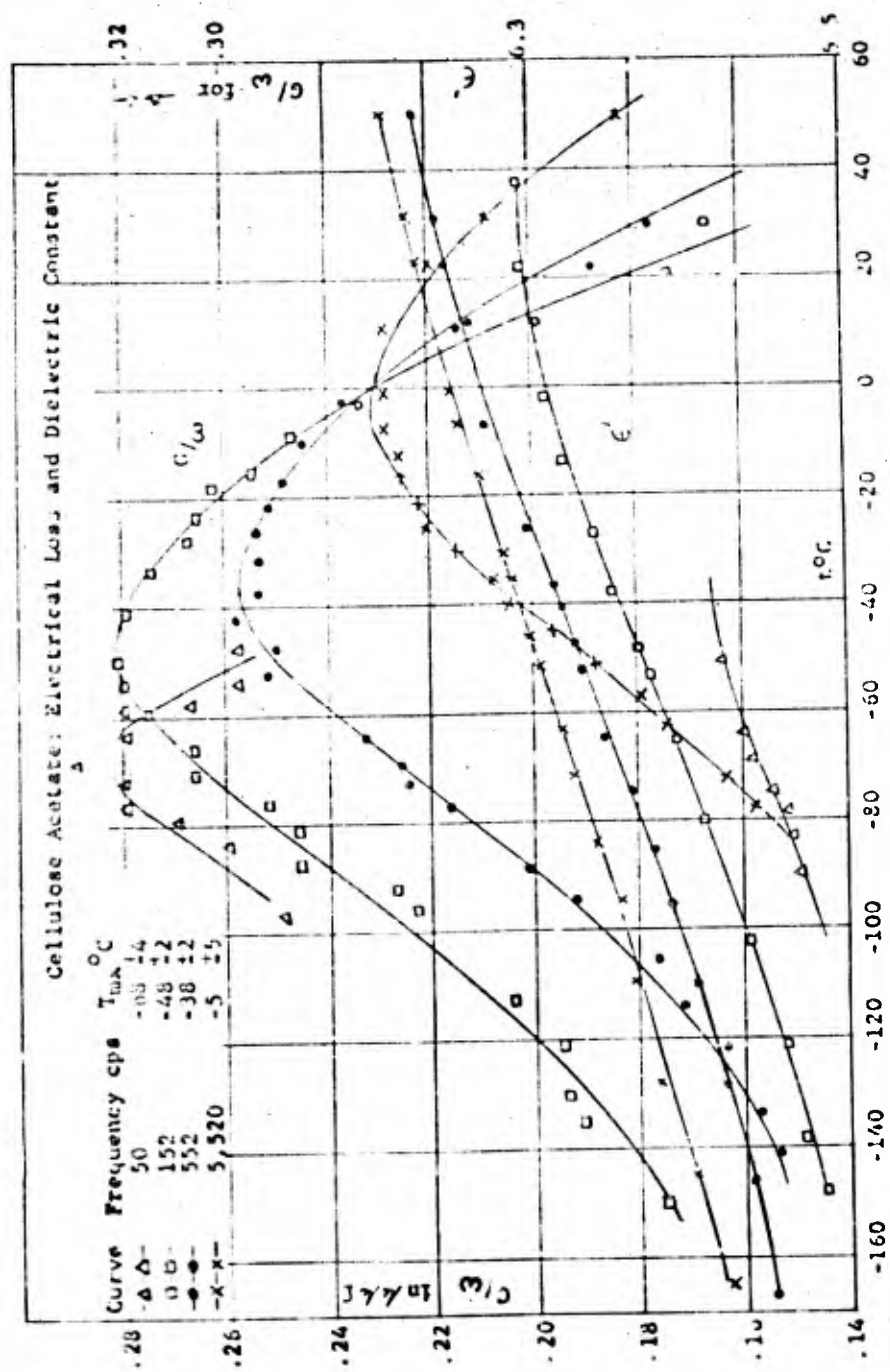


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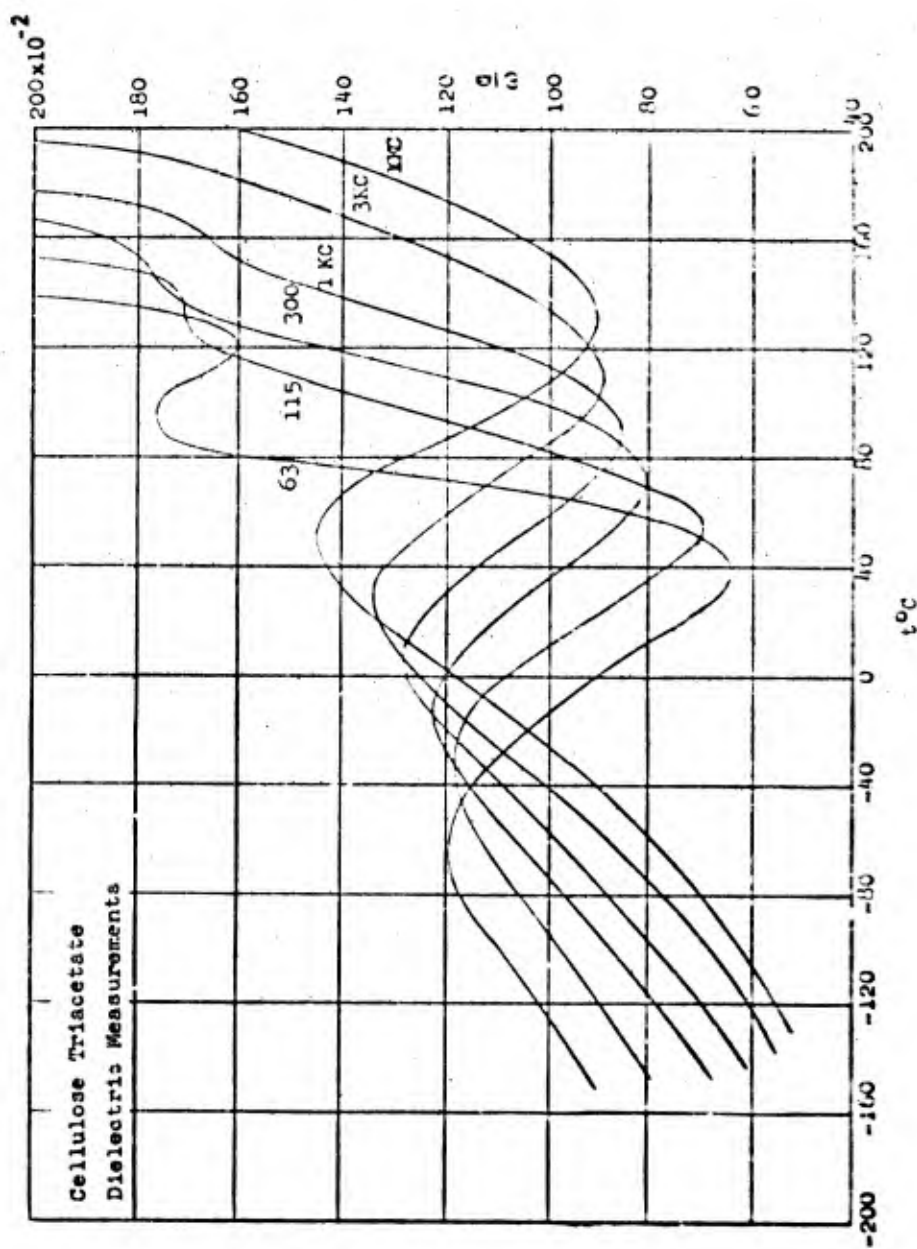


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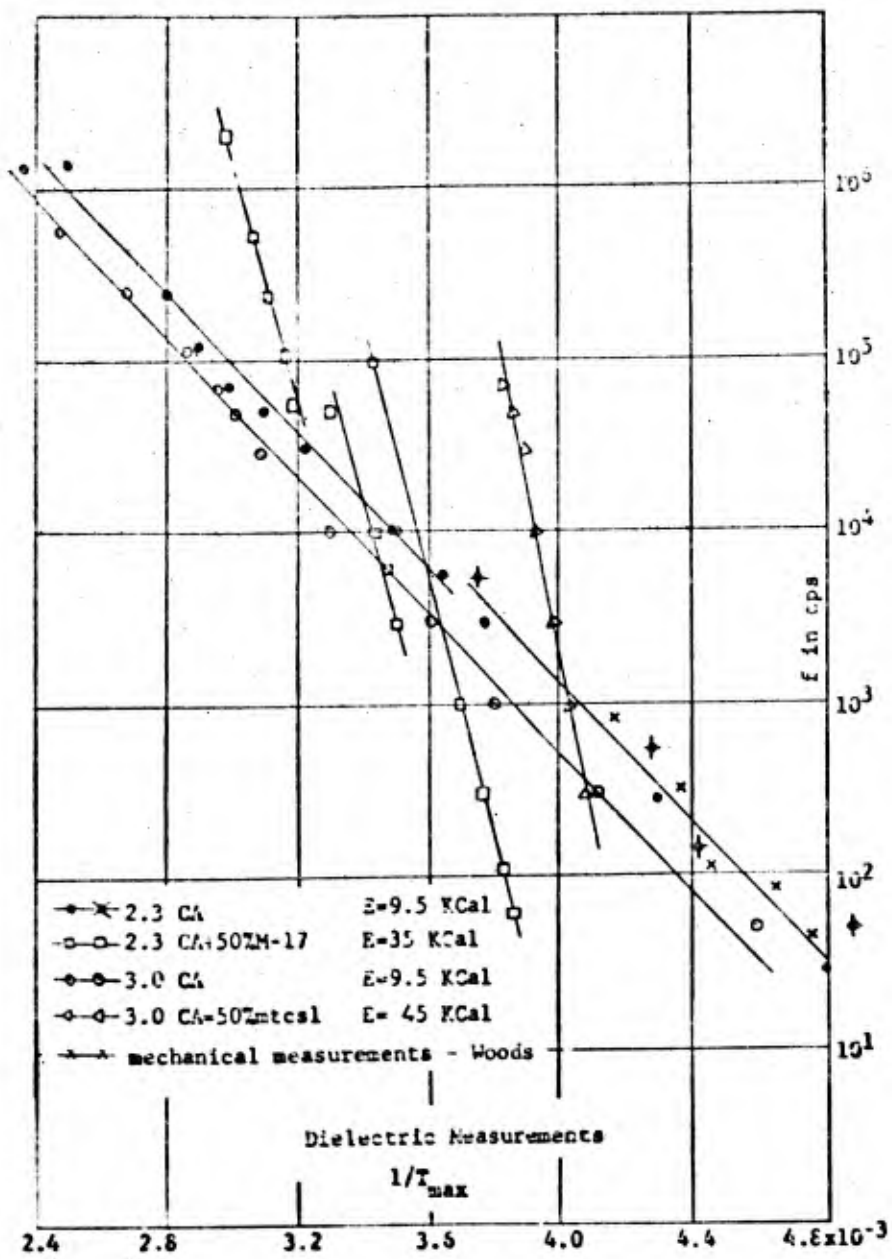


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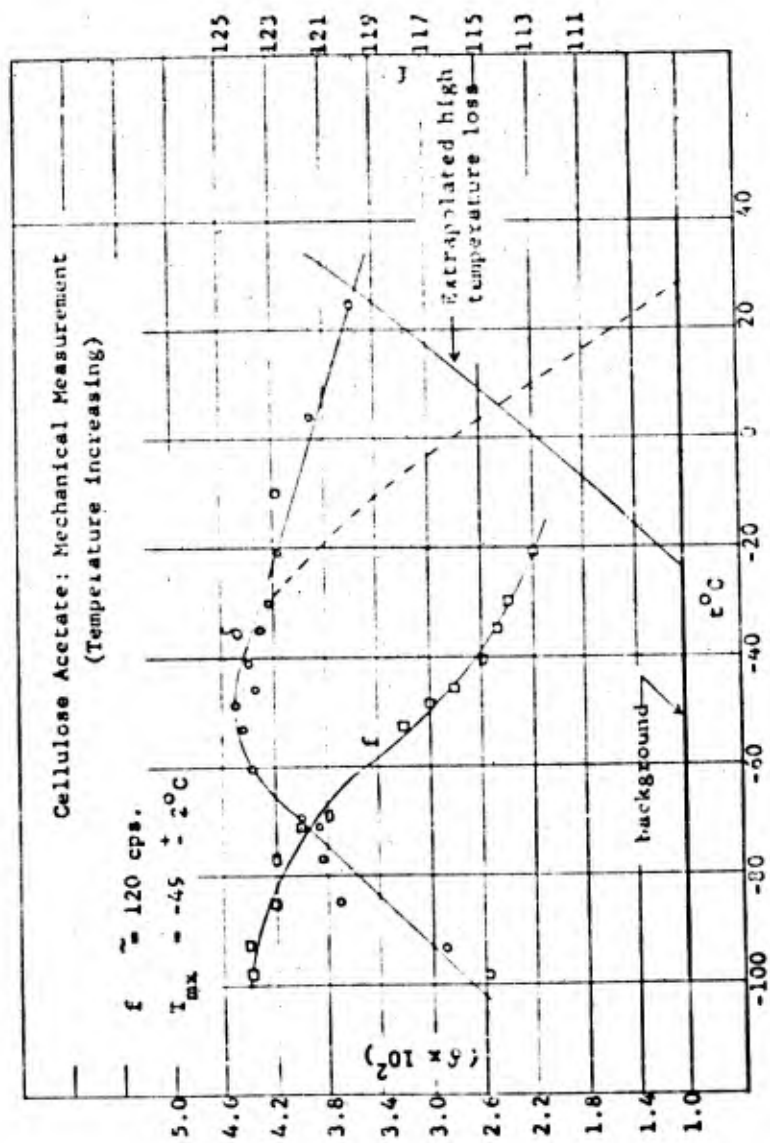


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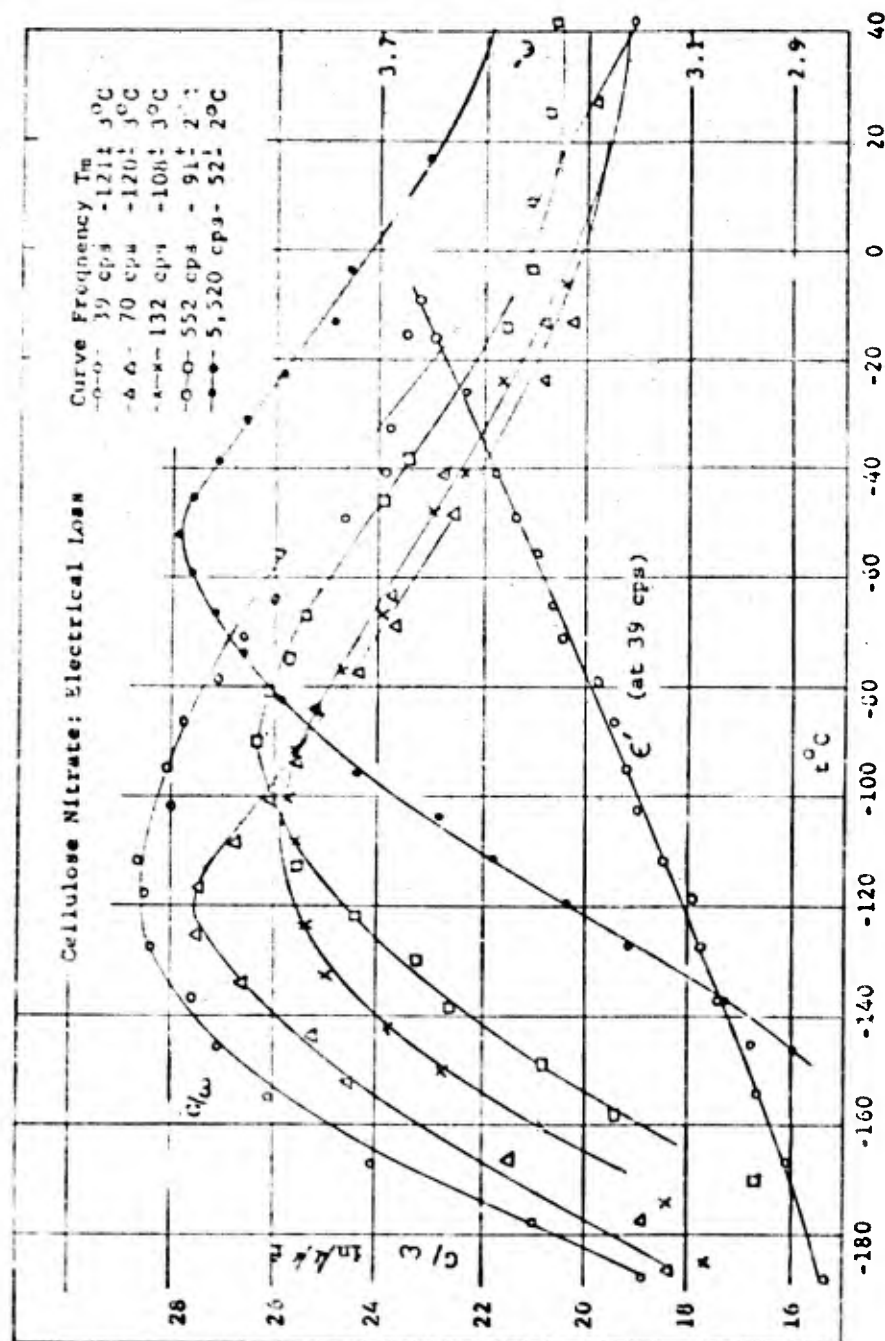


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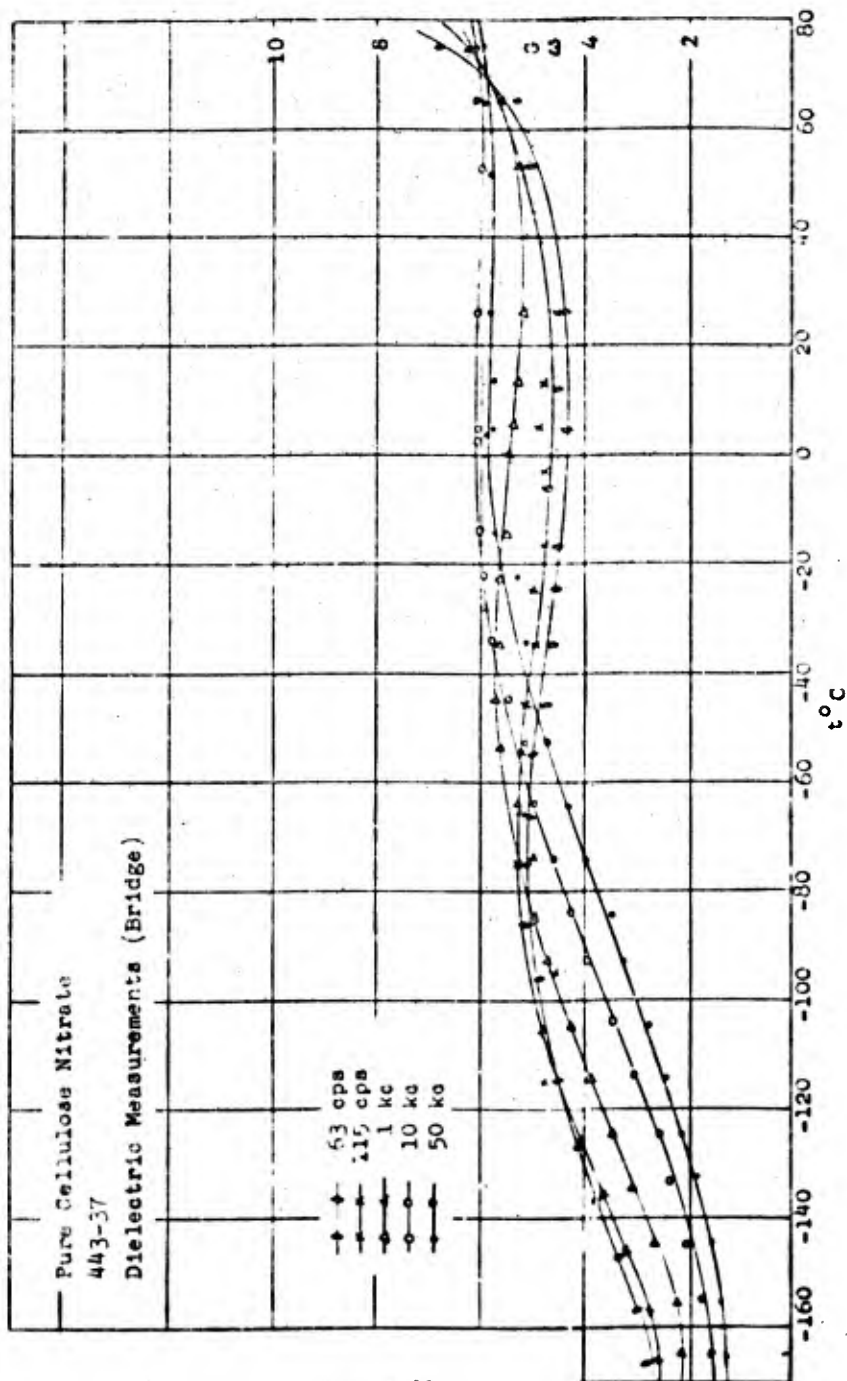


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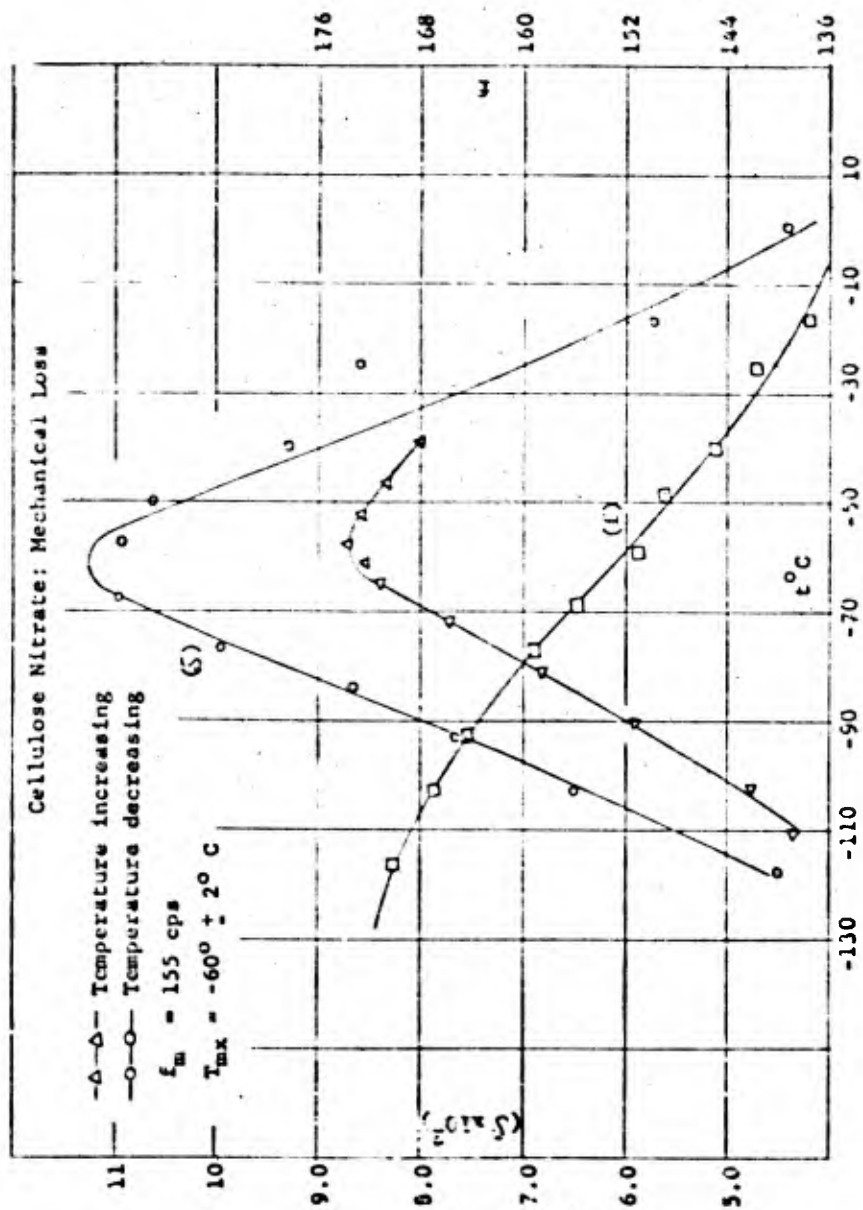


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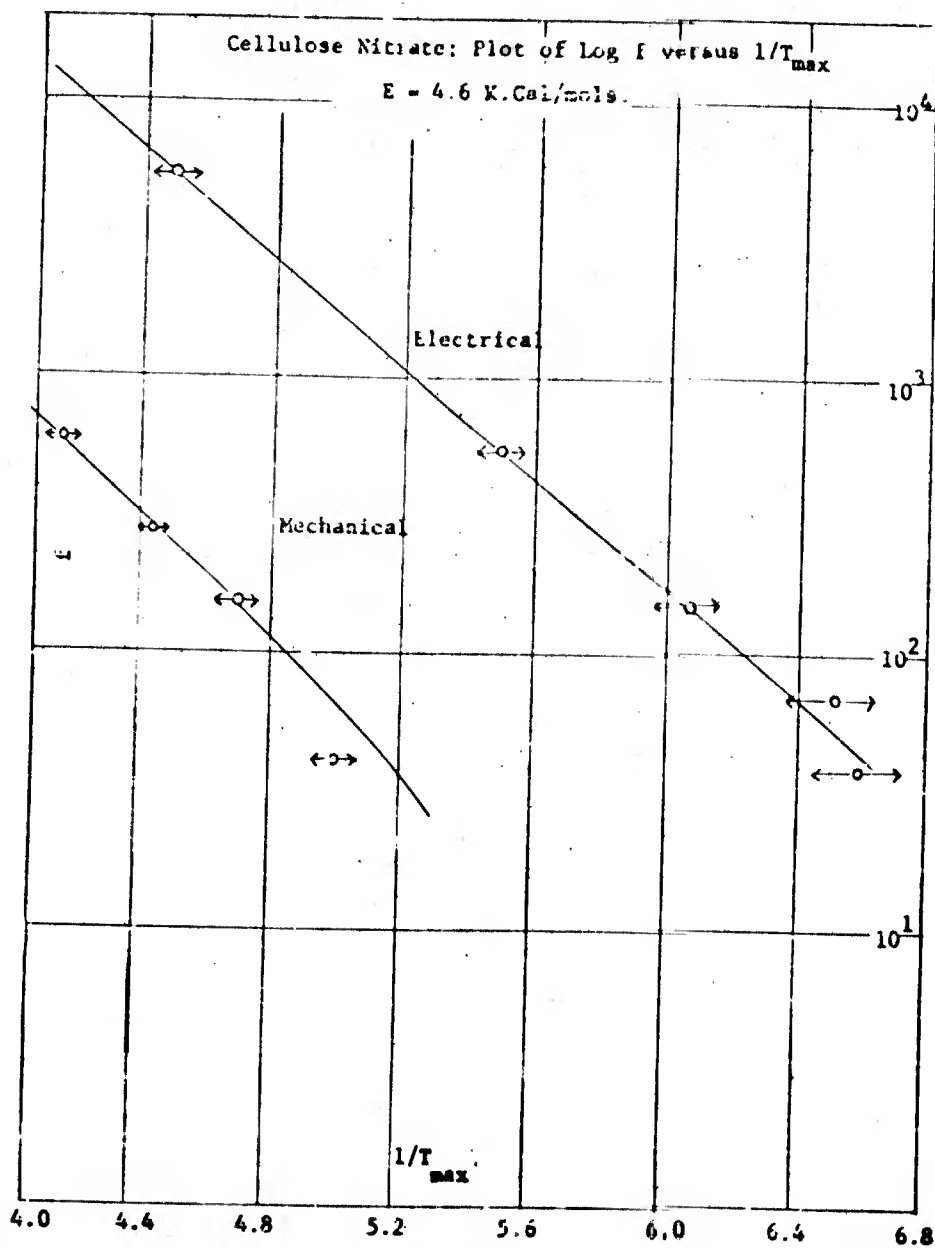


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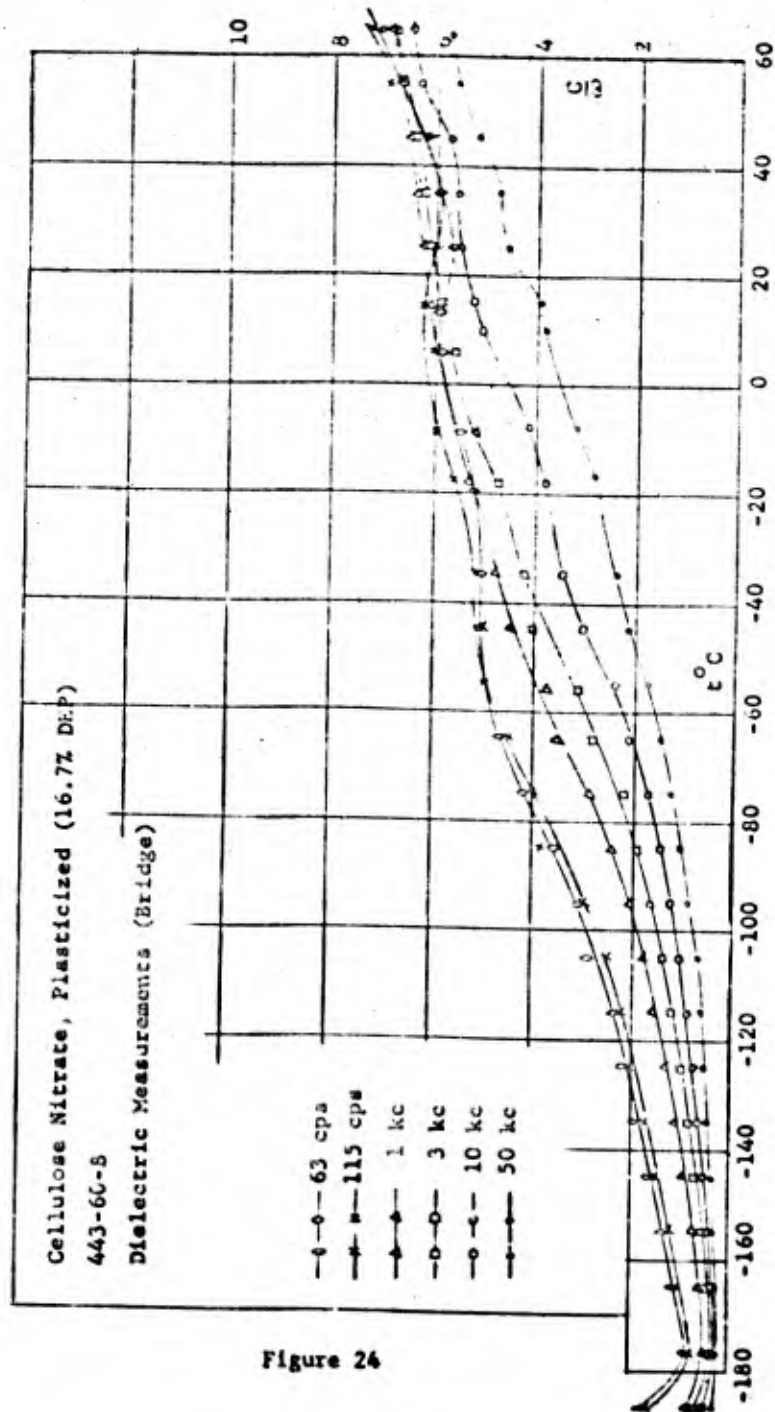


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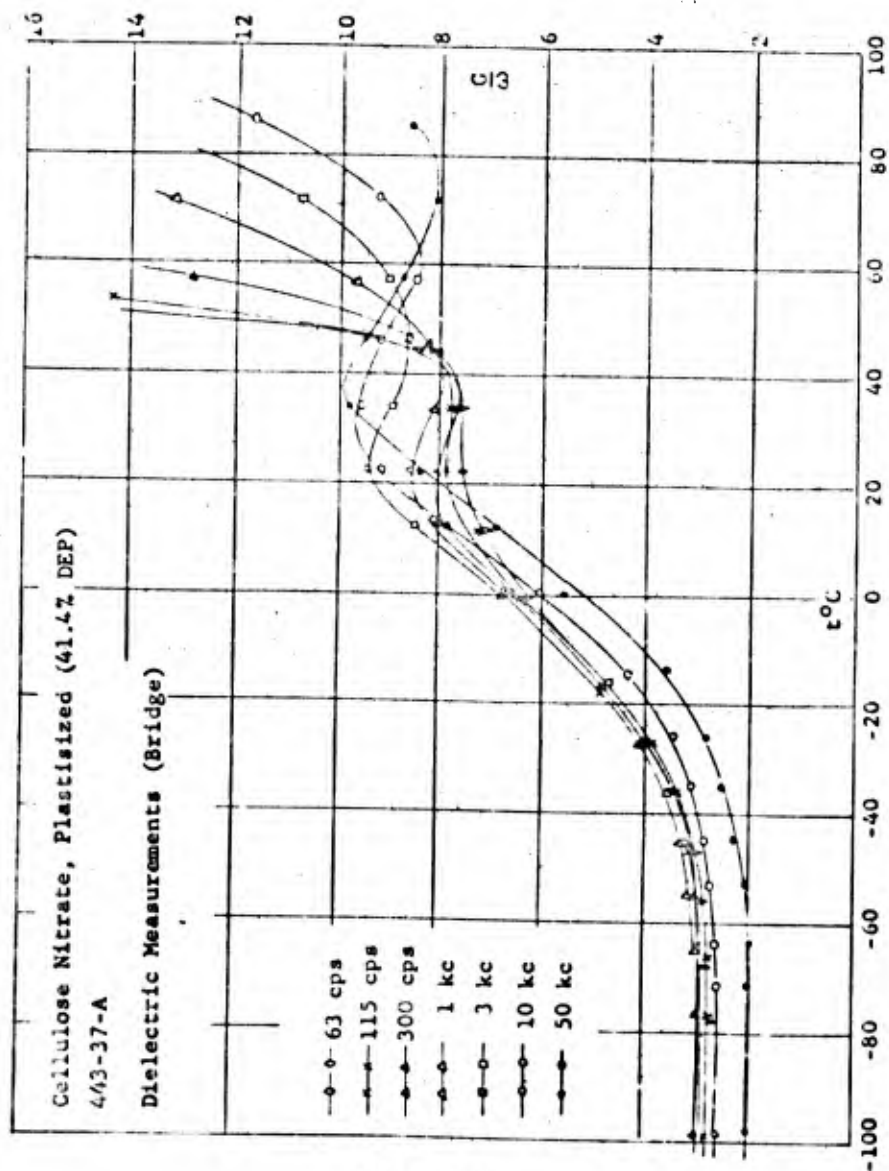


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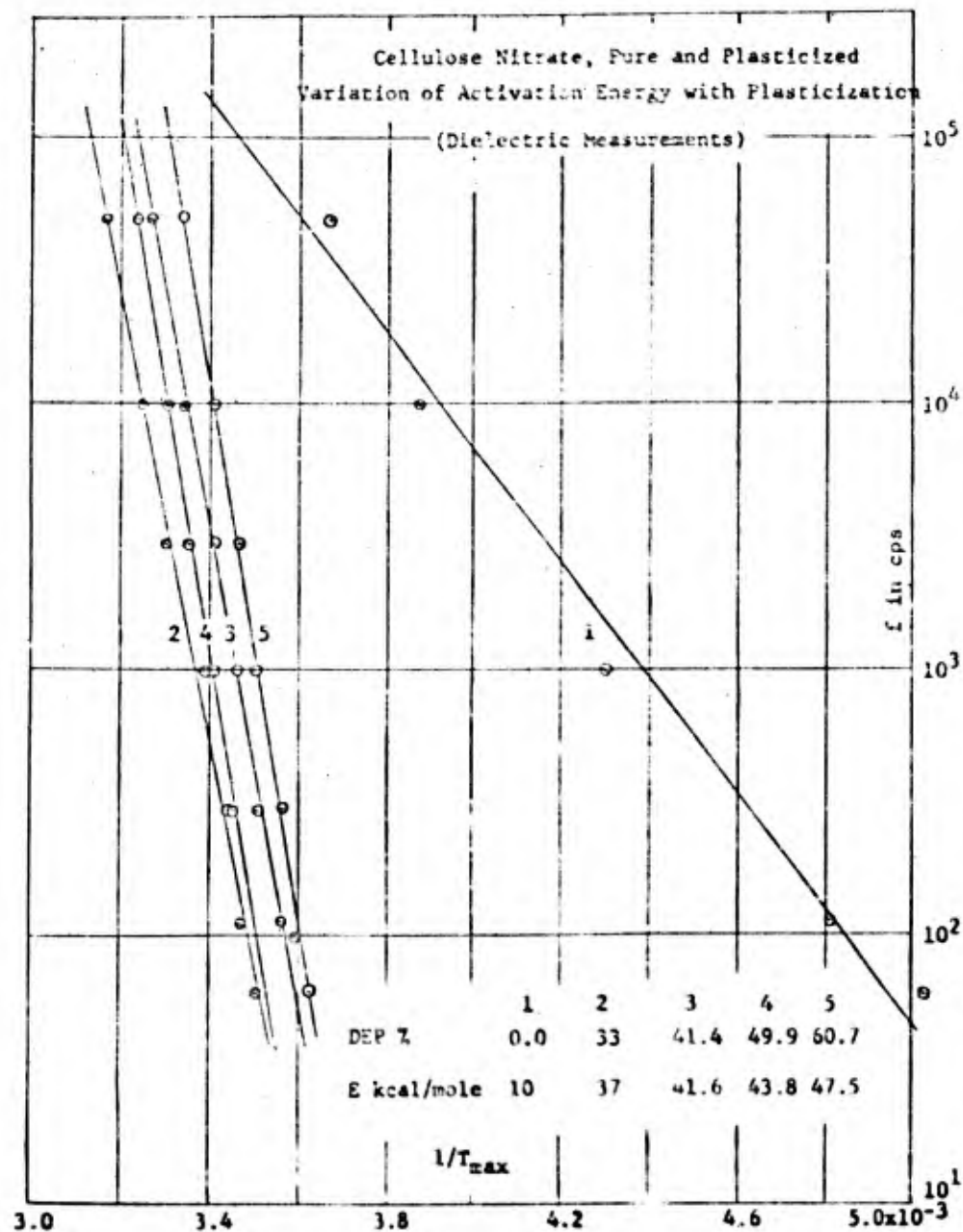


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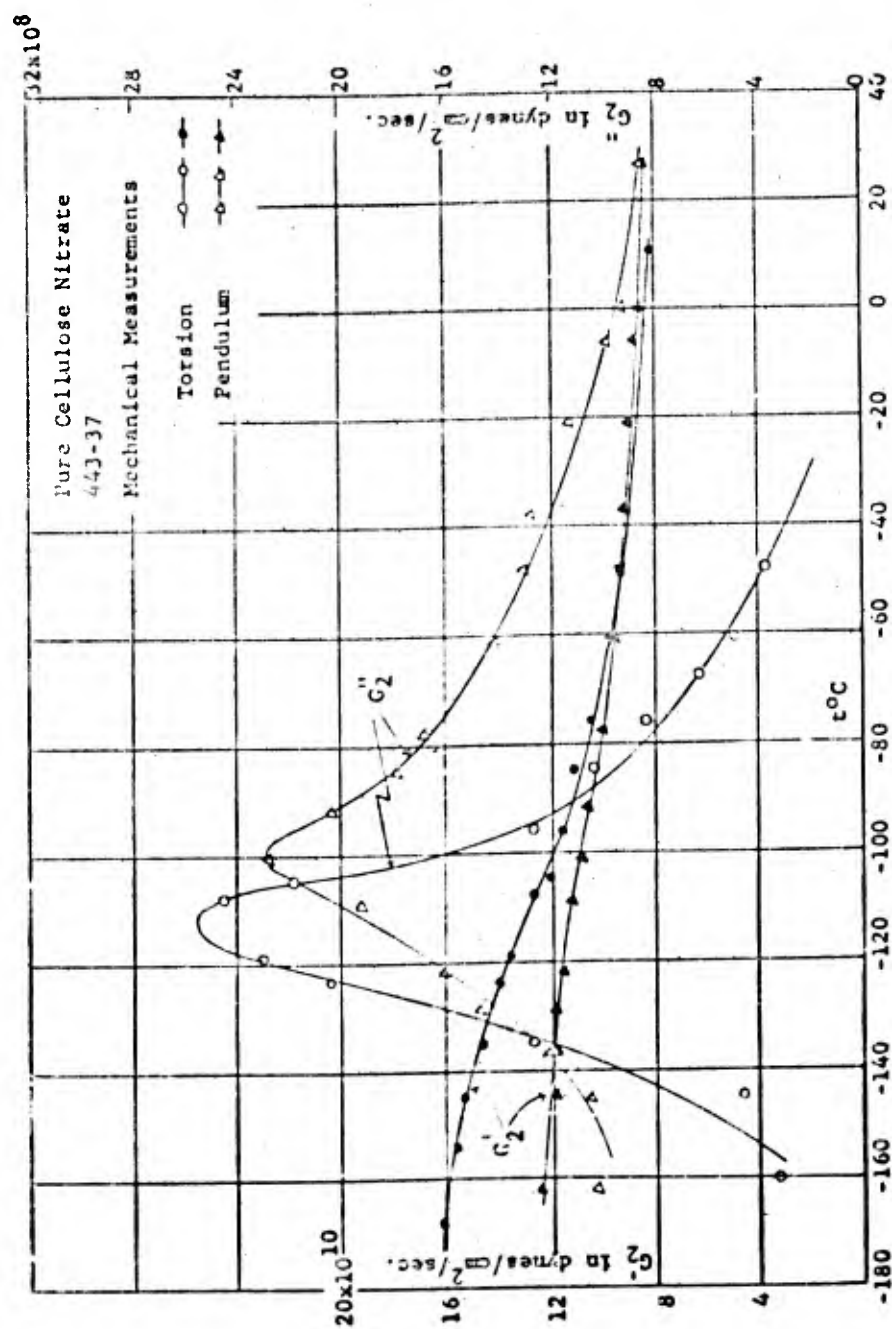


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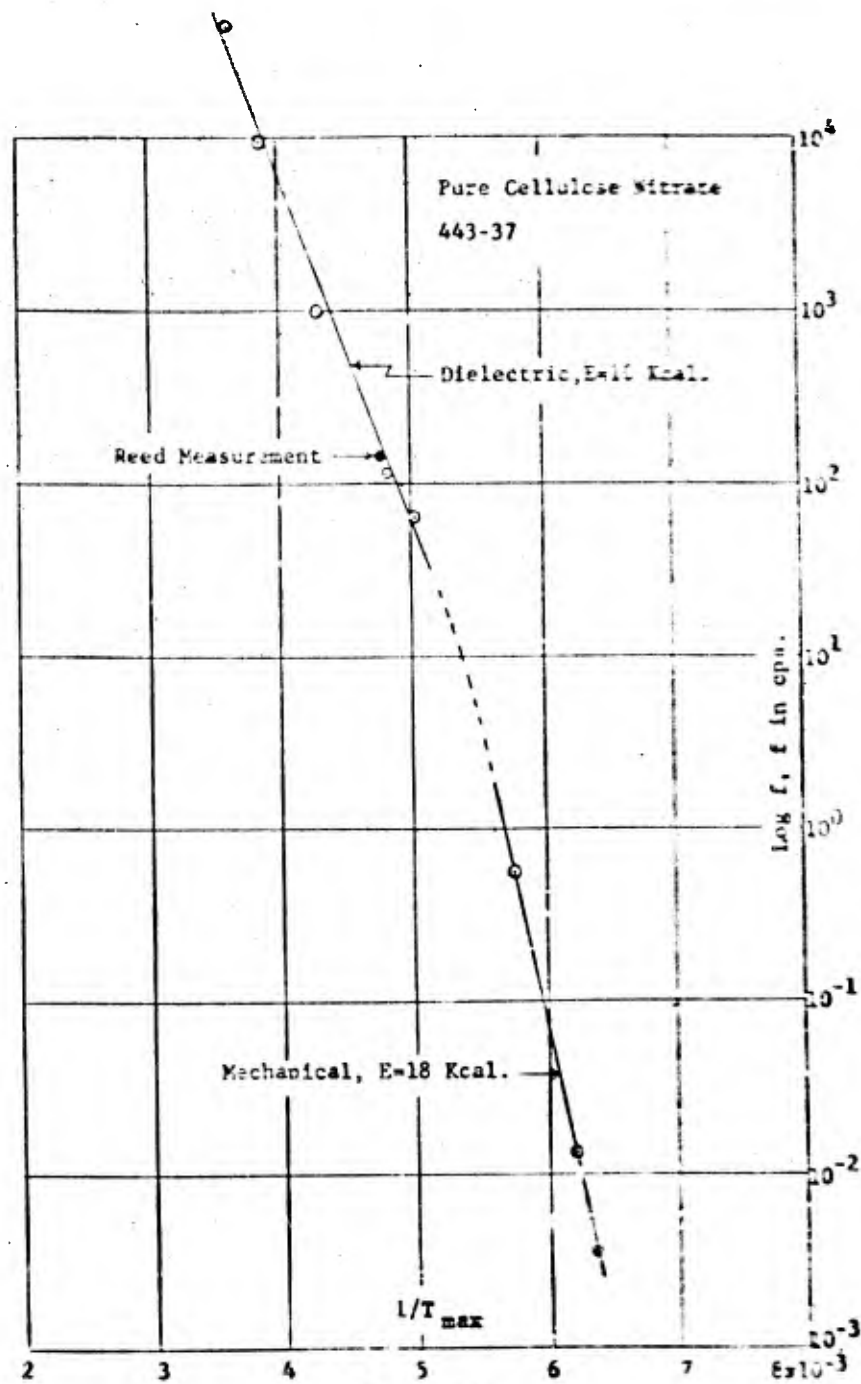


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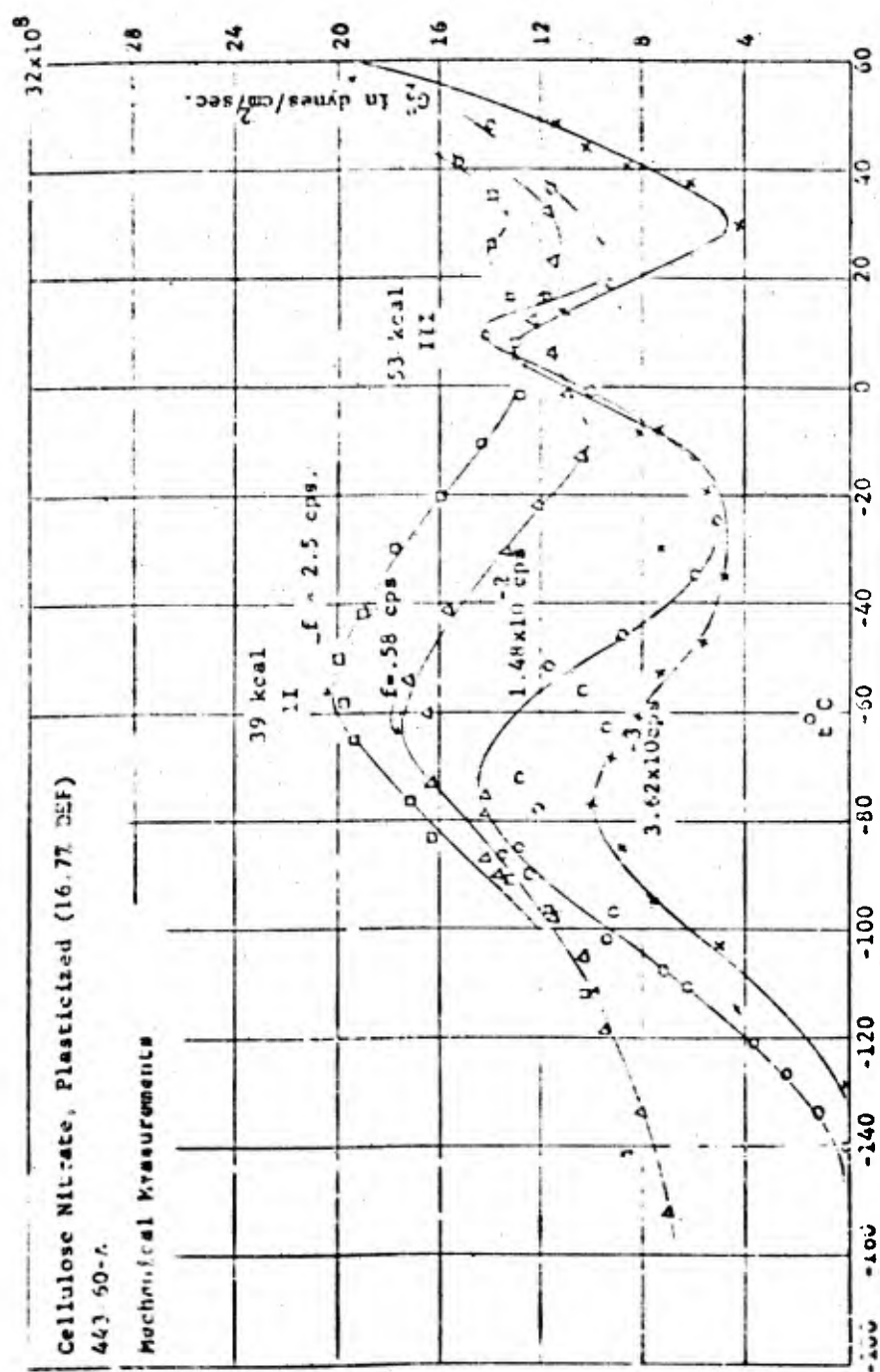


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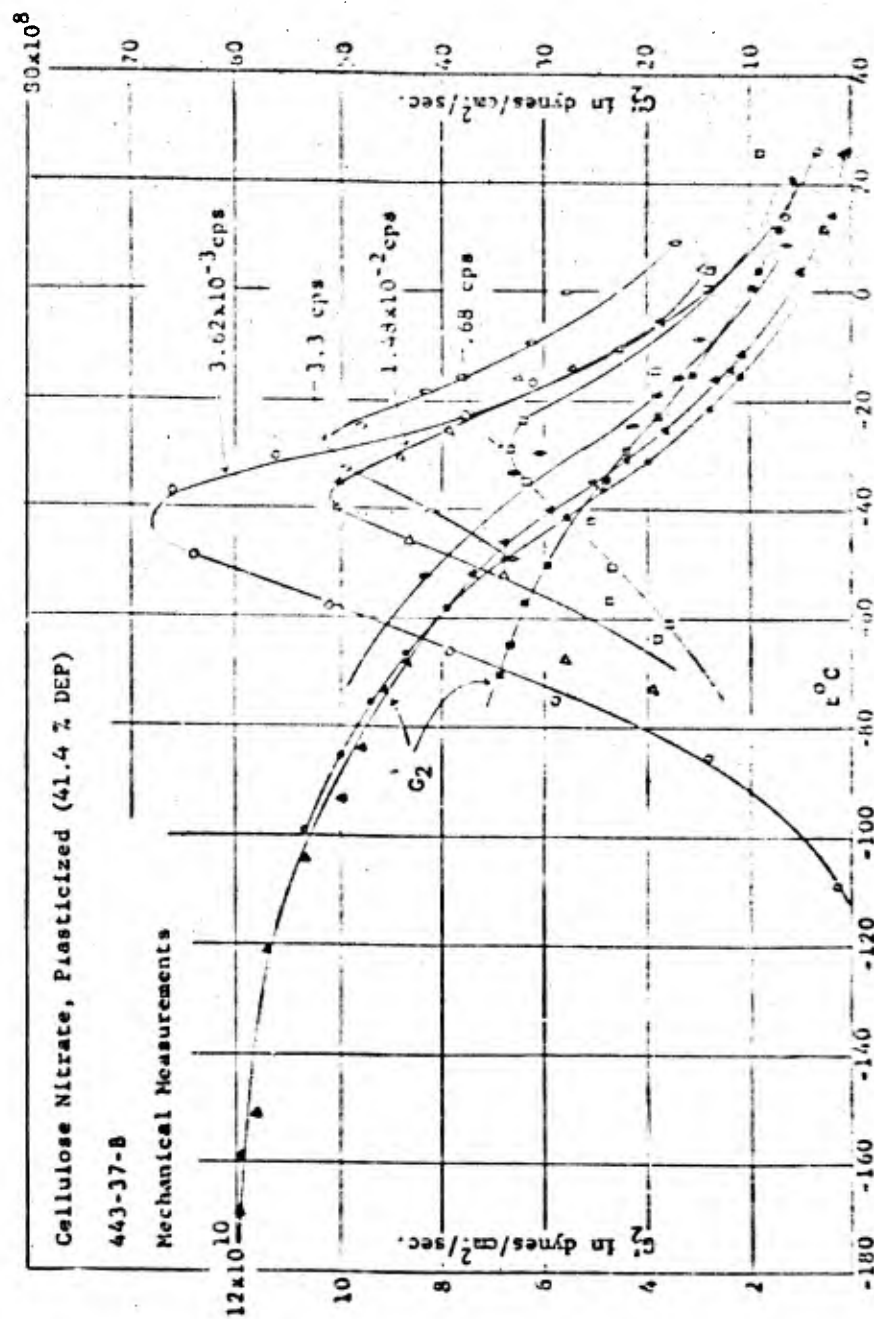


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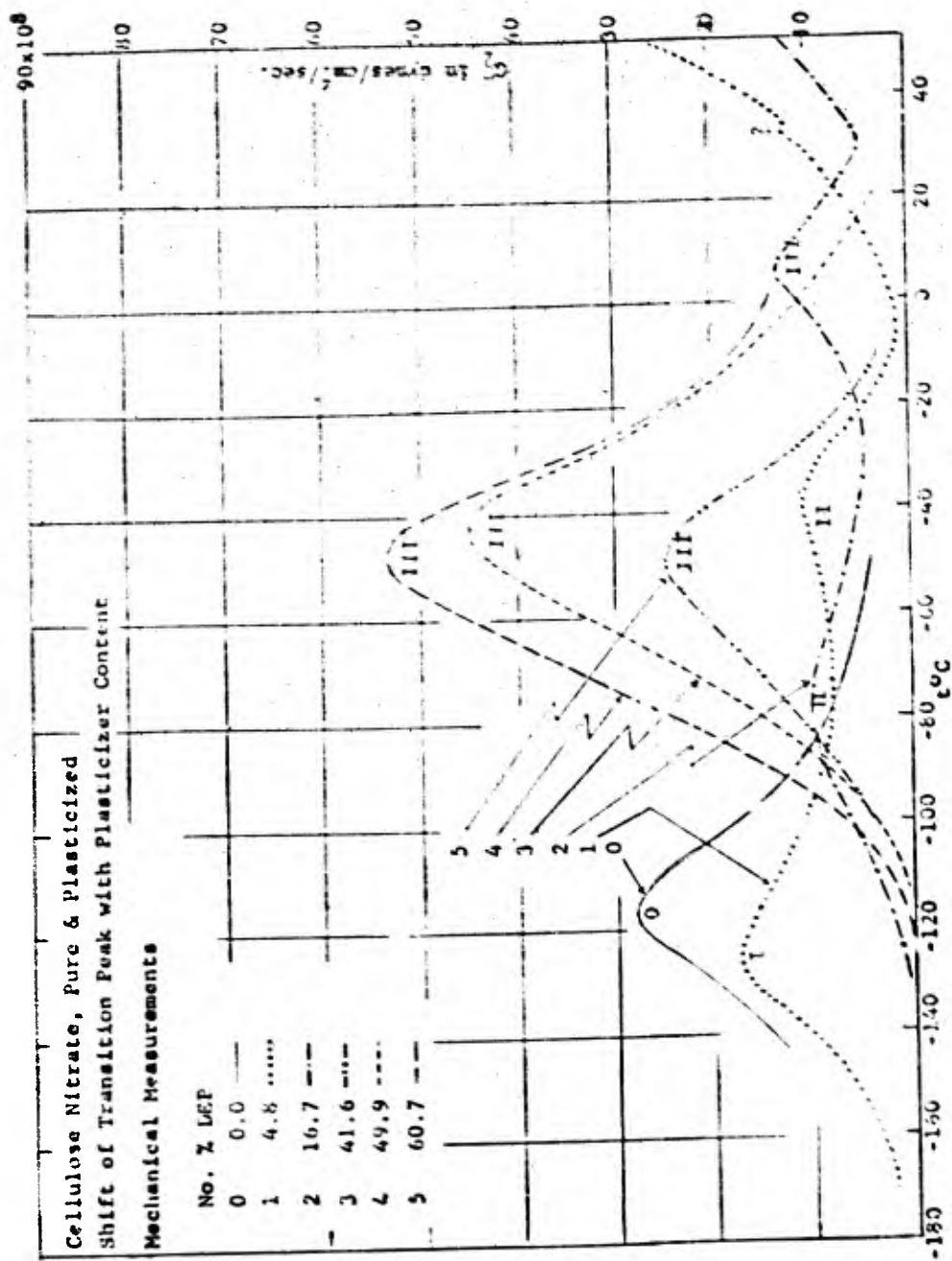


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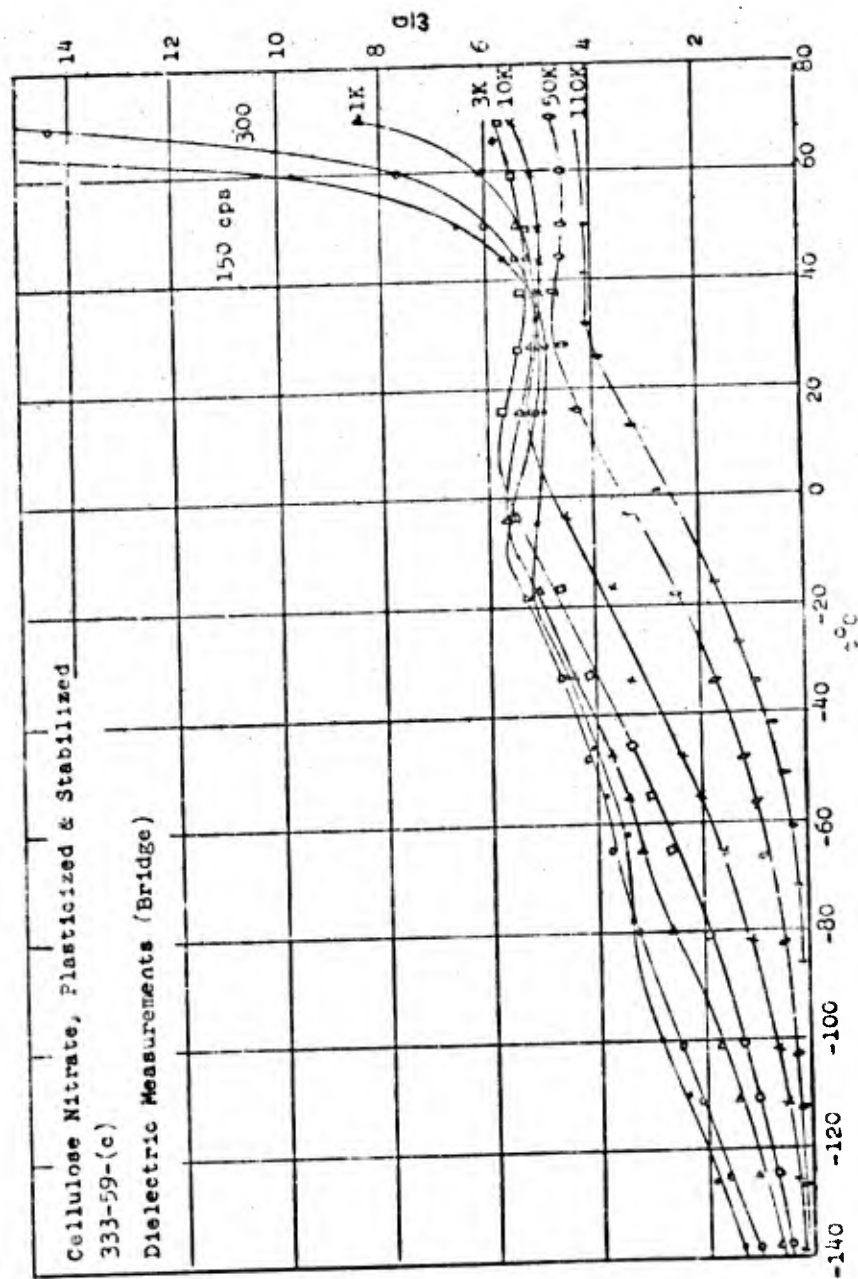


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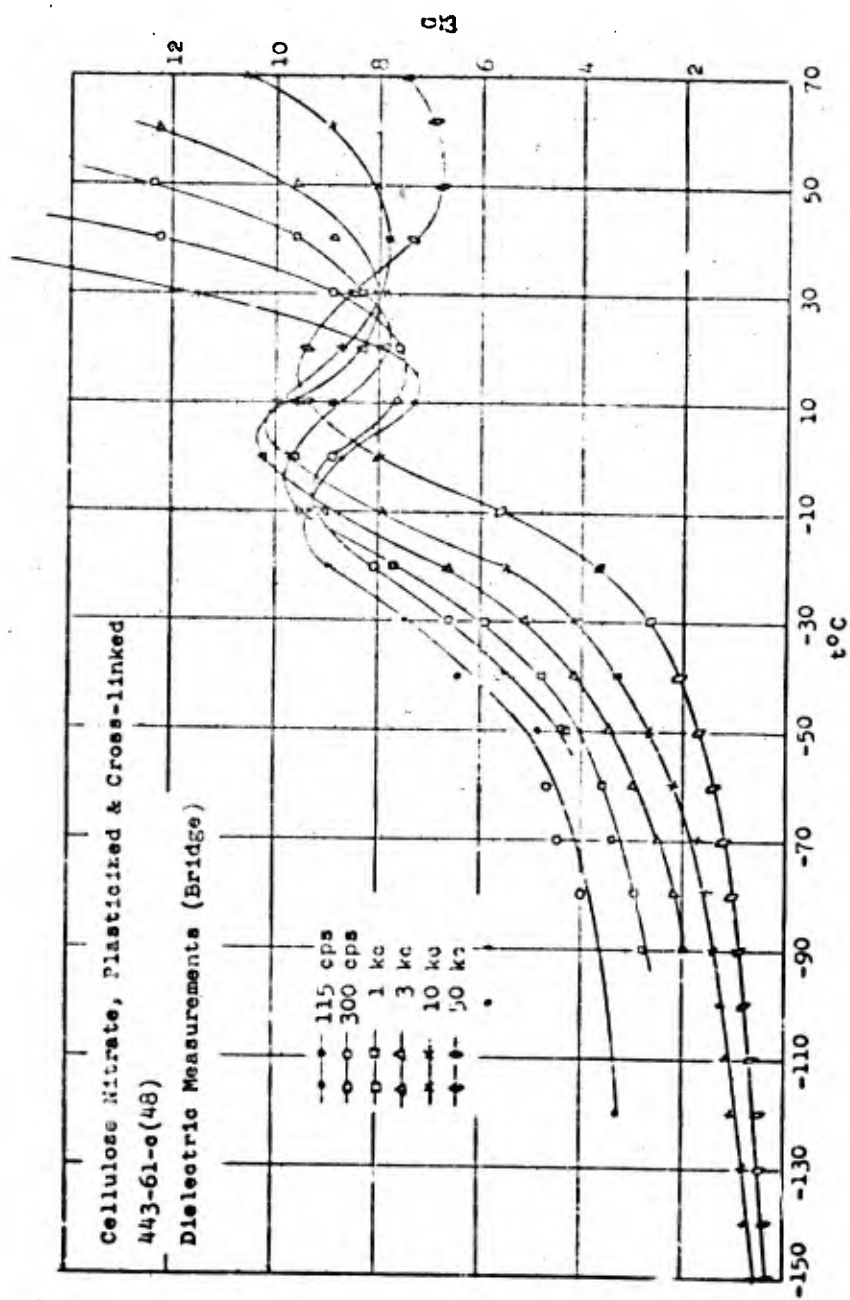


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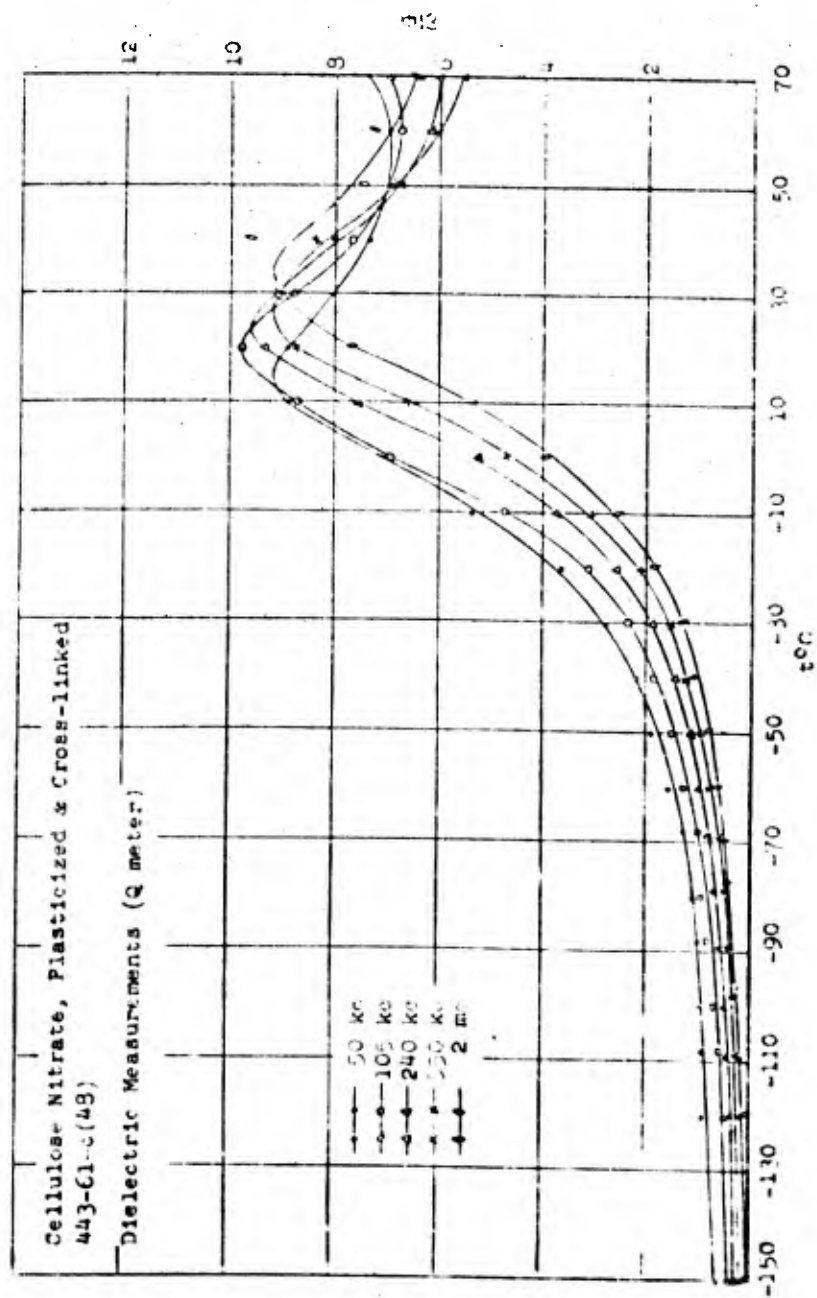


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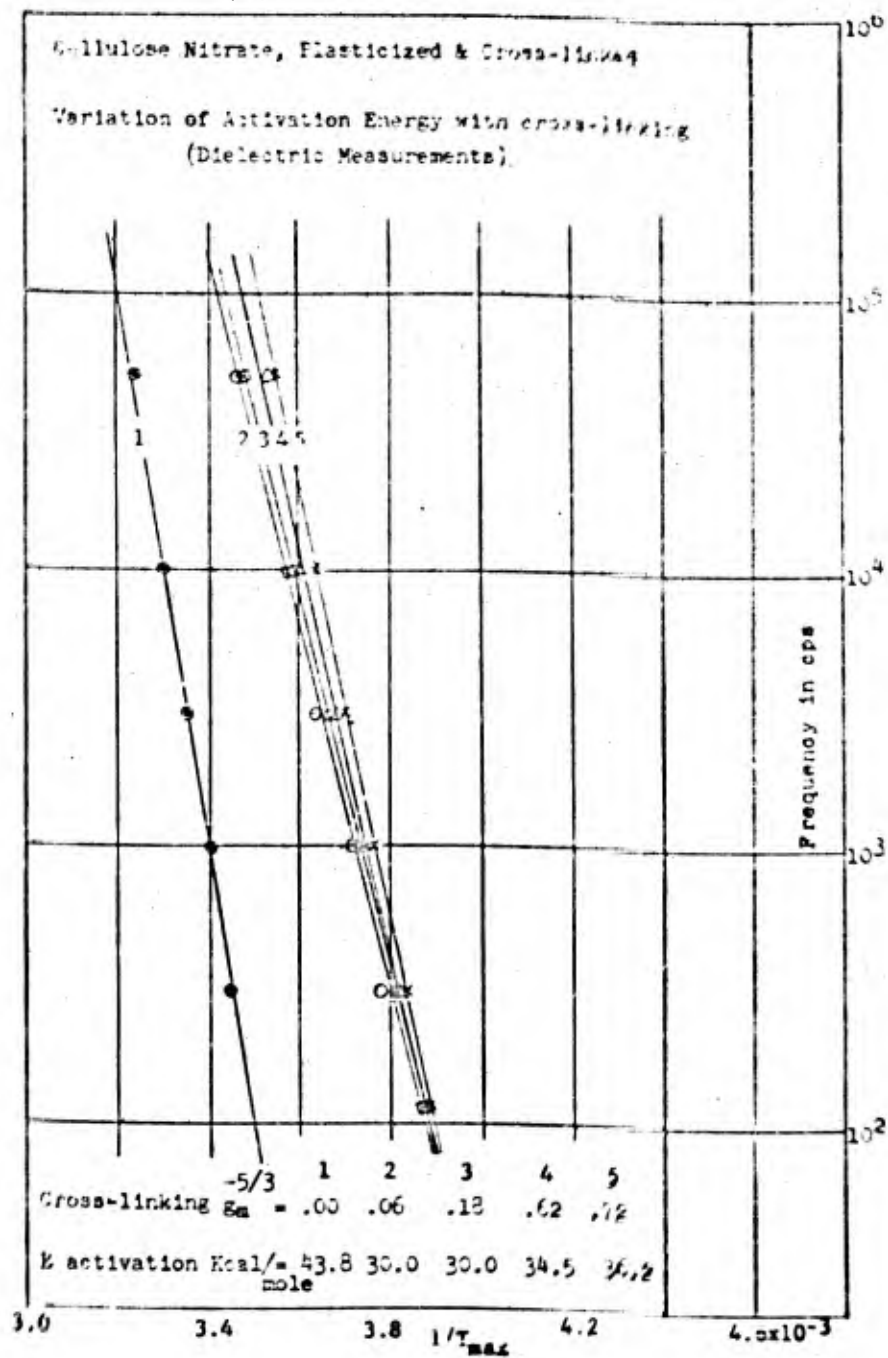


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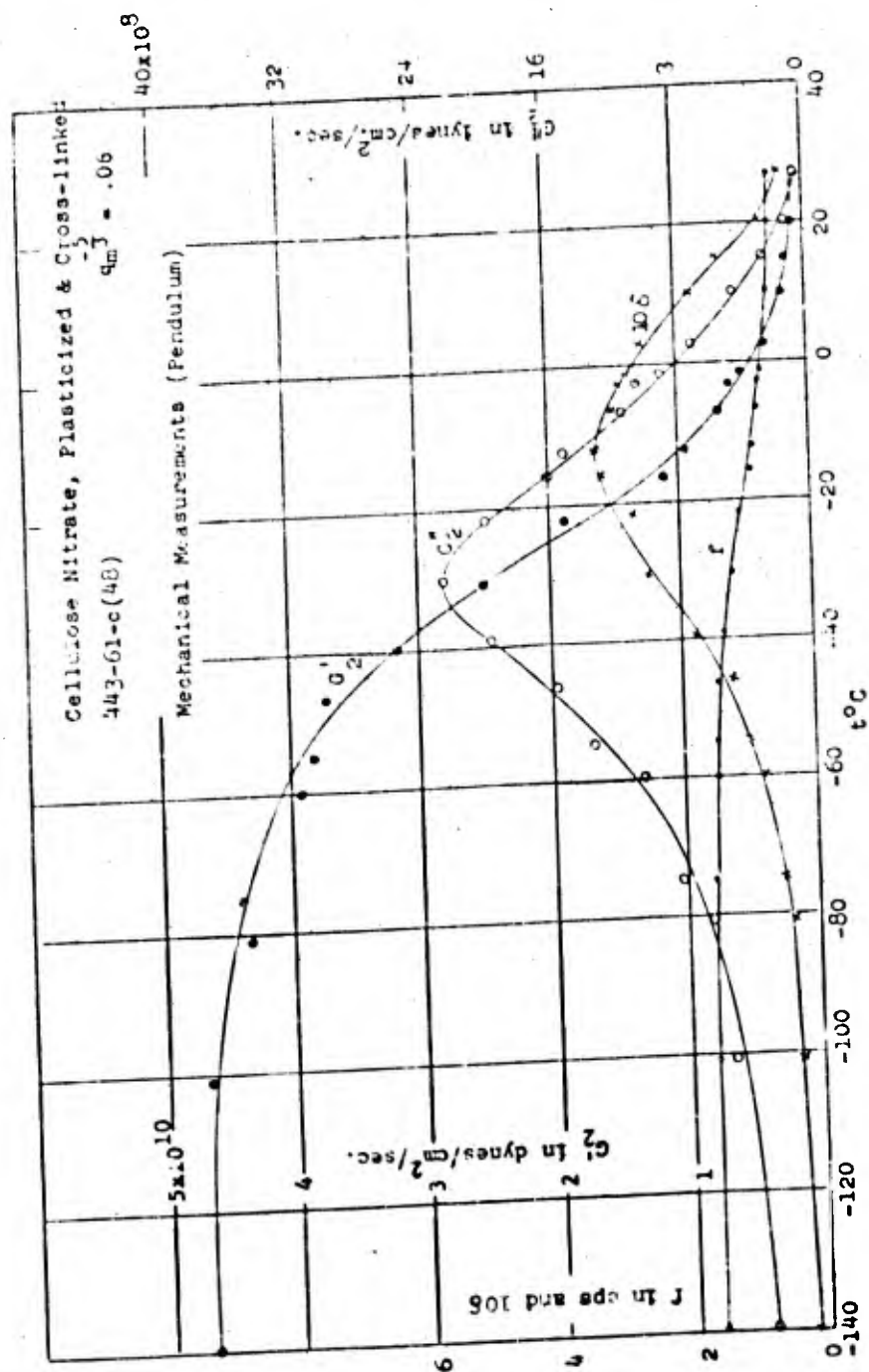


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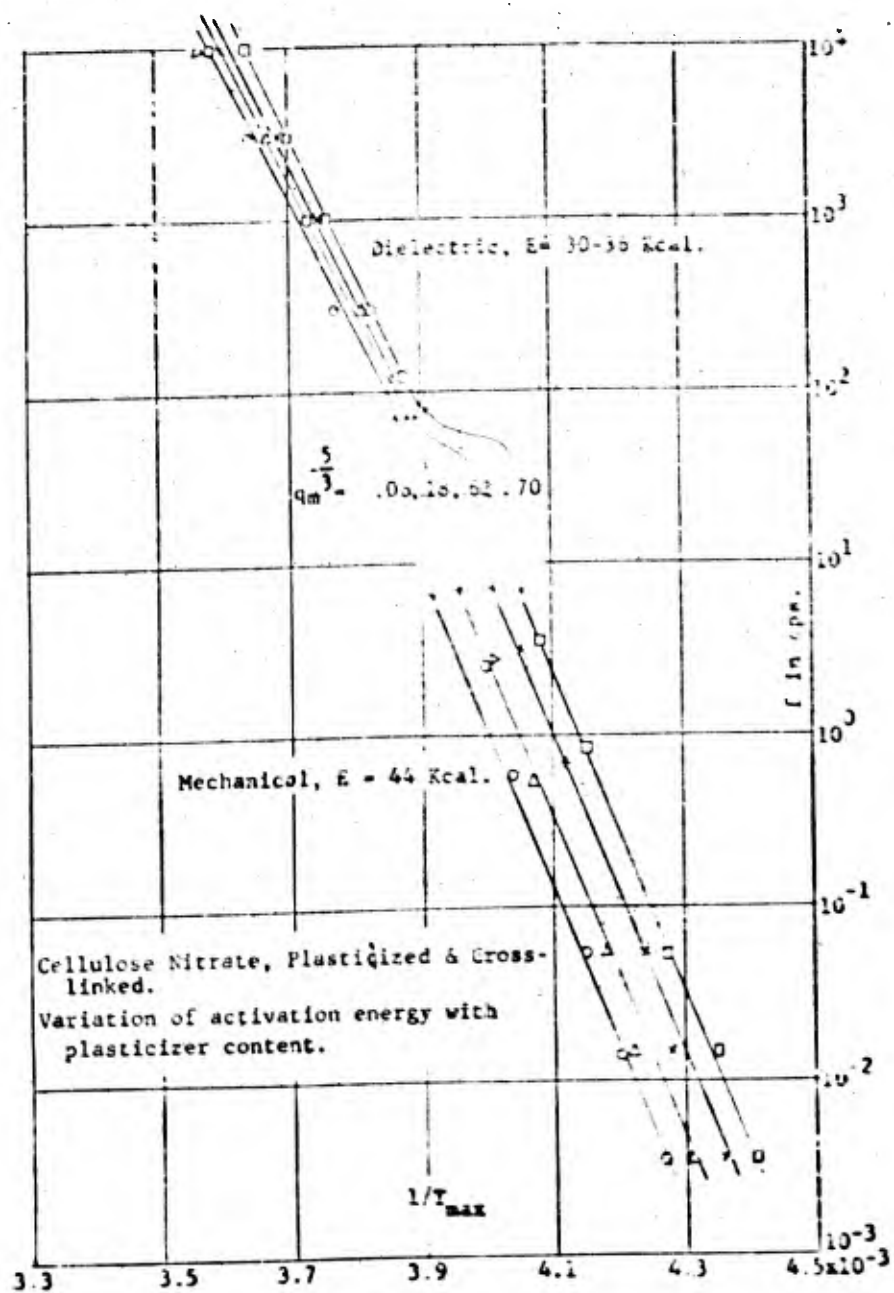


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